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THE LIME-SILICA SERIES OF MINERALS.[1]

BY ARTHUR L. DAY AND E. S. SHEPHERD.

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ANY ONE who has followed the work of the eminent Norwegian scientist, Prof. J. H. L. Vogt, during the past three or four years, must realize that an extraordinarily effective weapon has come into the service of petrology, the full power of which cannot at once be understood or appreciated. We refer to the methods and established generalizations of physical chemistry. The older science of chemistry has made such strides under these new theories of solutions that we really have little more to do than to apply them ready-made to our own problems, like a smooth and powerful machine tool of guaranteed effectiveness. Mineral solutions are after all only chemical solutions over again with slightly different components and a different, a very different range of temperatures and pressures.

It has been the purpose of this laboratory to attempt this task by a direct application of the principles and methods of quantitative physics and chemistry, or, in a word, to study mineral and rock formation by direct measurement at the temperatures where the minerals combine and separate like the solutions of ordinary chemistry under ordinary conditions. We further determined, wherever possible, to prepare chemically pure minerals for this purpose in order that such conclusions as we might reach should not be dependent upon dangerous assumptions regarding

[1] An extract from a paper of the same title read before the American Chemical Society at Ithaca, June 28, 1906.

the harmless character of the 5 or 10 per cent. of "impurities" not infrequently present in hand specimens from natural sources. It is at once obvious that in order to succeed the first experiments must be restricted to the simplest reactions and that these will not always be the most important or the most interesting, but the results will always be in definite terms and final when the materials used are pure. Furthermore, the accumulated experience obtained from simple cases will safely and surely lead to successful methods of a scope to meet the more complicated problems of rock formation.

This plan was really entered upon several years ago in a very small way and with very limited resources. The first paper,[1] which was published in 1904–5, contained a laboratory study of a typical isomorphous pair, the soda-lime feldspar series, carried out in the spirit of the above plan. The second,[2] which appeared in February of the present year, was a very careful study of enantiotropic mineral inversion between the mineral wollastonite and the pseudohexagonal form which has been obtained by several observers but which appears not to have been found in nature. The present paper, which is the third of the mineralogical series, undertakes to carry through a fairly complete set of measurements upon a typical eutectic pair—the lime-silica series. It is still incomplete in some particulars, notably at the ends of the series. Mixtures very rich in lime possess temperature constants which are beyond the reach of existing apparatus, while on the silica side the extreme viscosity and consequent inertness which were encountered in the soda feldspars effectually veil or prevent the development of the phenomena which occur there. Some approximate measurements have been made even in these regions (represented by dotted lines in the diagram, Fig. 2), but they have not the same accuracy as those portions of the curve which are represented by full lines. All the mixtures used were prepared with the greatest care and were chemically pure within one or two tenths of 1 per cent.

Lime-Silica Minerals.—In the lime-silica series only one well-defined mineral is known—wollastonite, which when melted

[1] Arthur L. Day, E. T. Allen and J. P. Iddings: Am. J. Sci. 19, 93 (1905). Publications of the Carnegie Institution of Washington, No. 31 (1905).

[2] E. T. Allen, W. P. White and Fred Eugene Wright: "On Wollastonite and Pseudo-Wollastonite, Polymorphic Forms of Calcium Metasilicate," Am. J. Sci. 21, 89 (1906).

usually crystallizes in a pseudohexagonal form of the same composition. This mineral has already been carefully studied by Allen and White, and the relation between the natural mineral and its second crystal form thoroughly cleared up. Pursuing the conventional methods of reasoning, we might also expect to have an intermediate mineral for the trisilicic acid, $2CaO\ 3SiO_2$; an åkermanite analogue, $4CaO, 3SiO_2$; an orthosilicate, $2CaO, SiO_2$; and a tricalcium silicate, $3CaO, SiO_2$. All of these minerals are deducible from the various silicic acids. We have undertaken to prepare and study the entire series of mixtures of lime and silica.

Boudouard's Measurements.—So far as known there has been only one serious attempt to determine the constitution of this series of minerals.[1] According to Boudouard, the freezing-point curve for the lime-silica minerals consists of four eutectics and three maxima (compounds), the maxima corresponding to the metasilicate, the orthosilicate and the tricalcium silicate. Unfortunately, the method used by Boudouard was a very inaccurate one. He prepared small cones of the various mixtures and placed these in a furnace alongside of Seger cones. The furnace was then heated and allowed to cool down again, after which the crucible was opened and the cone observed to see whether or not the mineral had melted. It is a common method in industrial practice, but has rarely been thought accurate enough for original determinations.

This method is peculiarly unsuited for such investigations for several reasons: Suppose the mixture to contain an eutectic with a greater or less excess of one of the components. The cone would begin to weaken as soon as the eutectic began to melt, and its further progress would be governed entirely by the relative quantity of eutectic present and its viscosity *after melting.* No information whatever regarding inversions in the solid or of the component in excess could be obtained, and errors of more than 500° would certainly occur (in fact did occur in Boudouard's case) in the interpretation of the softening temperature in some parts of the lime-silica curve. Let us illustrate by a perfectly obvious hypothetical case (Fig. 1): Assume first that the freezing-points change rapidly following a steep liquidus *AB* (see also Fig. 2, Curve *DE*). The amount of eutectic in concentrations *X* and *Y* will be so great as to soften the cone long before the

[1] Boudouard: J. Iron and Steel Inst., 1905, p. 339.

freezing-points Z and W are reached. If, on the other hand, the liquidus slopes gently (AC), the amount of liquid eutectic as compared with the solid phase is smaller and the temperature of softening of the cone will approximate more closely to the change in freezing-point.

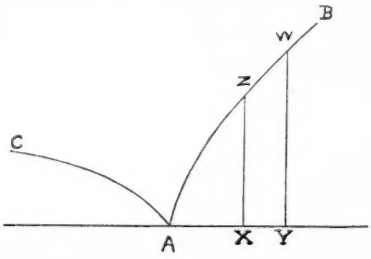

Fig. 1.

Furthermore, if the cones are made up from the initial components ($CaCO_3$ and SiO_2 for example), the heat of combination is liberated as the cone approaches the melting temperature and raises the temperature of the cone above that of the furnace, producing sudden fusion, of which the neighboring Seger cone can receive no record.

Incidentally, one finds here the explanation of Hoffmann's experiments[1] on the temperature of formation of slags. Contrary to his statement that the "temperature of formation is above the temperature of fusion," just the reverse is true. Under normal conditions these mineral combinations occur at temperatures lower than the melting-point, the exceptions occurring only when the materials are so coarsely ground or poorly mixed that combination is retarded until the melting-point of the slag is passed. The orthosilicate of calcium is a very good instance of the formation of a compound below its melting temperature. We shall show later that while this compound melts at about 2080°, it is possible to prepare it below the melting-point of platinum, in fact in platinum vessels, by heating the finely ground material in the Fletcher furnace, regrinding, mixing, and reheating. By this process it is possible to obtain a compound which gives the optical tests for the orthosilicate and is entirely without free lime or silica.

[1] H. O. Hoffmann: Trans. Amer. Inst. Min. Eng. 29, 682 (1899).

Apart from the criticism which this particular application of cones appears to us to deserve, it is also well-known that the time factor is always very important in dealing with a Seger cone. Boudouard himself states (p. 343): "A very small difference in temperature or *a few minutes' additional heating*[1] often suffices for the softening stage to pass into one of complete fusion." If this statement was made understandingly, the method merited rejection by Boudouard himself. Furthermore, the use of Seger cones for exact work will always be unsatisfactory because it depends upon the judgment of the operator to say when a cone has "fallen" sufficiently to be considered melted, and different observers almost always obtain widely different results under like conditions. As has been pointed out by Day and Allen,[2] any method of measurement which is not based upon some reasonably sharp physical change must be expected to give different results in different hands. Suppose this method were to be applied, for example, to the determination of the melting temperature of orthoclase or albite, or even pure quartz, which have been shown to possess a viscosity entirely comparable in magnitude with the rigidity of the solid crystalline mineral; almost any conclusion could have been reached under these conditions.

It is stated by M. Boudouard that all mixtures of lime and silica between 30 and 90 per cent. of lime melt below 1500°. This certainly cannot be the case. Pure orthosilicate of calcium when heated in a platinum crucible will stand without showing the slightest trace of melting while the platinum containing vessel melts down. The temperature must therefore be at least as high as the fusion point of platinum (1720°). We found no lime-silica mixtures richer than 60 per cent. in lime which could be melted in platinum vessels.

Apart from the uncertainty in the temperature measurements offered by Boudouard, we shall also undertake to show in its proper place that there is no pure lime-silica compound corresponding to tricalcium silicate. We are therefore somewhat at a loss to explain in any satisfactory way how the published curve which has attracted so much attention in England, was really obtained.

In this kind of investigation it is always desirable to begin with

[1] Italics are ours.

[2] Loc. cit.

a careful determination of the physical properties of the pure components, although in the present case it must be admitted that this was the most inaccessible and difficult portion of the field over which we worked.

Lime.—Calcium oxide melts at a temperature so high that it is not yet possible to make a satisfactory determination of its melting-point. It can be fused in the electric arc under favorable conditions to a clear liquid of low viscosity which crystallizes readily into a well developed cubic structure. Near its fusing temperature, lime either becomes quite volatile or the carbon of the arc reduces it to the metal which volatilizes and is immediately reoxidized outside of the heated zone. We are unable to offer conclusive evidence in favor of the one hypothesis or the other, but the fact that pure lime at 2000° shows no signs of a high vapor pressure points rather to the second explanation as the correct one.

For experiments with lime fusion, we obtained some artificial graphite,[1] practically free from all impurities, so that no contaminating substance was introduced into the fused lime from the electrodes. To further guard against possible contamination, only that part of the cake which formed above the (horizontal) arc was used in determining its physical properties.

Density of Lime.—The density of fused calcium oxide was determined as follows: A selected portion of the crystalline mass was finely ground, ignited to drive off adsorbed water, and weighed in carefully dried turpentine after the method of Day and Allen. The results are not in very good agreement, due to the difficulty of weighing out the product without its becoming superficially hydrated or absorbing carbon dioxide.

Fused CaO. H_2O at 25° = 1.
3.313
3.307
3.329
Mean density, 3.316 (25°)

This crystallized lime is much less readily attacked by water than is the amorphous oxide. It is, however, not indifferent to water. Five grams of the crystals when ground and mixed with a small quantity of water in a test-tube scarcely raised the tempera-

[1] Prepared especially for us by the International Acheson Graphite Company, Niagara Falls, N. Y.

ture at all, but upon standing for some five minutes, the charge exploded with considerable violence. Unpowdered blocks of the crystalline oxide when placed in cold water dissolved slowly without appreciable heating. Hot water attacks them more rapidly, but the action of the water is slow in both cases when compared with the amorphous lime.

The hardness, according to Mohr's scale, is between 3 and 4.

Silica.—The melting temperature of silica has been variously estimated from 1200° to 2000°, but so far as known no careful determination of it has ever been made. Since this oxide melts to an extremely viscous liquid, attempts to determine the melting temperature by observing the softening of the charge are wholly misleading. The molecular deorientation proceeds very slowly, extending over a considerable range of temperature, as albite and orthoclase have been found to do,[1] but with the disadvantage that this temperature region is too high to be reached with a thermoelement and no other method of temperature measurement possesses sufficient sensitiveness in this region to locate the melting temperature by the heat absorbed during slow fusion. Determinations of the freezing-point are out of the question, owing to the inertness of the viscous melt.

An approximate determination of the melting temperature was made in this way: A gram or two of finely powdered quartz was placed in a small iridium crucible and heated in an iridium tube furnace.[2] Experience has shown that melting and inversion phenomena in very viscous substances take place much more readily if the material is finely divided. A tiny fragment of platinum foil was then laid on the top of the charge and the furnace slowly heated until the foil was observed to melt. Upon removing the charge from the furnace and examining it microscopically, evidence of fusion was found throughout the mass. The crystal grains had inverted to tridymite and the superficial liquefaction had caused them to sinter tightly together, but no displacement of the grains had taken place. At the temperature of melting platinum, therefore (1720°), silica shows positive evidence of fusion. Other similar charges were then prepared

[1] Day and Allen: Loc. cit.

[2] No detailed description of the apparatus used or the methods of operating it can be included in this brief abstract. They are nearly all accessible in other publications from this laboratory or in contemporary pyrometric literature.

and the operation repeated with longer exposures and temperatures slightly below the melting-point of platinum, the temperatures being measured with a Holborn-Kurlbaum optical pyrometer[1] focused on the platinum fragment. By repeating this process at short temperature intervals and with about twenty minutes' exposure, melting was definitely established as low as 1625°.

The iridium furnace is unfortunately not adapted for long-continued heating, and the platinum coil furnace will not reach this temperature, so that an effort to discover a definite temperature below which the solid is stable and above which it will melt, if given time enough, was abandoned. If the heating is moderately rapid, the crystalline solid will persist far above the melting-point of platinum; if slow enough, it liquefies completely at 1625° or even lower. It is probably a fair assumption that pure crystalline silica begins to melt at about 1600°,[2] and will continue to complete fusion, if given time enough—above that point the higher the temperature the more rapid the melting. A charge of quartz was heated for a long time in a platinum furnace at 1550° without producing a trace of fusion.

There is little satisfaction in pursuing an inquiry of this kind. As has been stated elsewhere with reference to an entirely similar case,[3] the term "melting-point" does not appear to be well applied to cases of this character in which the crystalline structure persists for days or weeks at temperatures above the point where melting begins. If the change of state is to be defined by the

[1] Holborn and Kurlbaum: Ann. Physik. 10, 225 (1903).

[2] In a recent number of this Journal (July) Mr. Alexander Lampen publishes an experimental determination of the melting-point of a "piece of pure quartz" as follows (five minutes exposure):

Edges rounded..... 1650°
Fused ..... 1700°

Our experience inclines us to the belief that these temperatures are too low for the stages of the melting described for two reasons: (1) We found no crystalline quartz fragment upon which rounded edges could be observed from without the furnace after five minutes' heating even at the temperature of melting platinum (1720°), a fixed point in which great confidence can be placed; (2) if Mr. Lampen was able clearly to see incipient melting through red glass within his furnace, as he has stated, the radiation which he measured cannot have been "black" and his instrument *must* have read too low.

This note is added by request since the reading of the paper.—THE AUTHORS.

[3] Publication 31, Carnegie Institution of Washington, p. 74 (3).

absorption of heat, and the absorption of heat extends over a wide range of temperatures and conditions, our forms of expression should be revised somewhat to include these hitherto unrecognized cases.

Tridymite.—The relation between tridymite and quartz appears to be a simple one, although the literature of the subject is unsatisfactory. But few trustworthy observations have been recorded and the conclusions drawn from them are vague and contradictory. So far as known, quartz has never been crystallized as such from mineral fusions except where catalyzers were present. Tridymite has probably been obtained by several individuals through the accidental crystallization of fused silica vessels,[1] but no especial attention appears to have been given to the circumstances in which it occurs, and its identification has not aways been positive.

Like the melting temperature, the inversion of quartz to tridymite and the recrystallization of fused silica are very difficult phenomena to study, owing to the extreme inertness of the material, but a number of experiments have been successfully carried out which appear to clear up the situation, even though the inversion temperature cannot be determined with any great accuracy.

First of all, we heated a large charge of finely ground quartz and followed the temperature curve carefully from 400° to 1600°. It was found after the experiment that the quartz crystals had, for the most part, gone over into tridymite and the change in the volume accompanying the inversion had generated enough pressure to completely shatter the open platinum crucible which contained the charge. The change was so gradual, however, that no record of it appeared upon the thermal curve. Subsequent experiments in which we endeavored to change crystalline quartz into tridymite at lower temperatures were successful as far down

[1] Prof. Dr. L. Holborn, of the Physikalisch-technische Reichsanstalt, Dr. M. Herschkowitsch, of the firm of Carl Zeiss in Jena, Dr. Küch, of the firm of Heraeus in Hanau, and the Rev. Theodor Wulf, S. J., formerly of Göttingen, in the preparation and use of quartz glass vessels, have noticed that the glass devitrifies at high temperatures in the presence of water vapor or after long usage. So far as we are aware, all of these observations have remained unpublished. Hahn, in the Int. Cong. f. angewandte Chemie, Berlin, 1903 (Vol. I, p. 714), notes the devitrification of a quartz glass tube at 1100°. He also identified the crystal formation under the microscope as tridymite.

as 1100°. To be sure, entire crystals showed no change whatever after six hours' exposure at 1400°, but powdered quartz is completely changed into tridymite after a few hours at that temperature. On the other hand, if finely divided amorphous silica, *i. e.*, fused ("quartz glass"), or better, precipitated silica, be allowed to remain for a short time at any temperature above 1000°, it changes promptly to tridymite—the precipitated material very rapidly, the quartz glass much more slowly. Neither the glass nor the precipitated silica ever crystallized as quartz at temperatures above 1000°, nor is there any difference in the optical properties of the tridymite obtained at the different temperatures, either from the quartz crystals or the amorphous silica. The rate of change is much influenced by the fineness of the powder, although there is no difficulty in crystallizing large blocks of solid quartz glass at the higher temperatures. In our experiments in the preparation of quartz glass,[1] we frequently obtained isolated spherulites of tridymite several millimeters in diameter, even with rapid cooling, which appeared to have been started by a grain of graphite or carborundum powder accidentally falling into the melt. On one occasion the entire block was coated with tridymite to a depth of a millimeter or more.

We have therefore succeeded, by direct experiment upon pure silica, in establishing the fact that tridymite, and not quartz, is the stable crystalline form of silica for all temperatures above 1000°.

At lower temperatures than this it is impossible, in view of the inertness of the substance, to obtain any further reaction, even with the finest precipitated silica, within the time available for a laboratory experiment. A month's exposure at 900° produced no change. We therefore followed the example of several distinguished predecessors in this field, and tried various catalyzers.

Formation of Quartz.—Hautefeuille thought he had produced quartz crystals by fusing amorphous silica with sodium tungstate at 900°, but the methods of high temperature measurement commonly employed in his time were very imperfect, and the temperature is undoubtedly too high. He has also stated that he obtained it by fusion with lithium chloride. Both Hautefeuille and Margotet have recorded the fact that in the presence of lithium chloride amorphous silica changes to tridymite at high

[1] Day and Shepherd, "Quartz Glass," Science, 23, 670 (1906).

temperatures and to quartz at low temperatures. We obtained quartz crystals from glass by the use of 80 per cent. potassium chloride and 20 per cent. lithium chloride, at all temperatures below 760°, while at temperatures of 800° and higher, only tridymite crystals appeared. The same results were obtained with vanadic acid and with sodium tungstate. The inversion point

quartz $\rightleftarrows$ tridymite

therefore occurs at about 800°. This conclusion is subject to the assumption that the inversion temperature is not lowered by the catalyzing agent—an assumption which seems to be justified by the fact that the quartz crystals obtained in this way (judged by the optical properties) appear to hold none of the reagent in solid solution.

The situation is, then, briefly this: Both quartz and amorphous silica at high temperatures change to tridymite. Quartz is consequently the unstable form of silica from 800° upward, and will go over into tridymite whenever conditions favorable to the change are present. The melting temperature of silica is therefore properly the melting temperature of tridymite and not of quartz as it is commonly described. We have once or twice succeeded, by extremely rapid heating, in melting quartz as such, or more correctly speaking, in carrying a quartz charge past the melting temperature of tridymite, melting a portion of it and finding a residue of quartz afterward which had neither inverted nor melted. It would hardly be possible by any known method, however, to obtain a separate melting temperature for quartz independently of tridymite.

The reverse operation, showing that tridymite inverts to quartz at temperatures below 760°, cannot be carried out in the laboratory without the use of catalyzers on account of the extreme slowness of the change. In the presence of 80 per cent. potassium chloride and 20 per cent. lithium chloride, quartz begins to appear from tridymite in quantities sufficient for positive identification after an exposure of five or six days at about 750°. No effort was made to invert the entire charge, on account of the slowness of the change and the fact that its character was now fully established. The glass crystallizes to quartz below 760° and to tridymite above 800°; crystalline quartz goes over to tridymite above 800°, and tridymite to quartz at 750°; the change is therefore enantiotropic and not monotropic.

Incidentally, a sufficient reason has been given for the complete failure of experimenters to produce quartz without catalysis. If dry silica at 900° is so inert as to undergo no reaction at all during a month's exposure under favorable conditions, how can we expect reaction below 800° where the viscosity is even greater? Silica must be crystallized below 800° to produce quartz.

Density of Silica.—The density of the quartz used and obtained in our experiments was determined with the following result, the aggregate impurity being not over one-tenth of 1 per cent.

Purified natural quartz.	Quartz glass.	H_2O at 25° = 1.
2.655	First preparation	2.209
2.653	" "	2.215
2.654	" "	2.212
	Second "	2.213
	" "	2.215
Mean, 2.654 (25°)		Mean, 2.213 (25°)

It will be noted that there is a difference of more than 16 per cent. between the density of the glass and that of the quartz crystals.

A charge of powdered crystalline quartz heated for several days at 1200° appeared under the microscope to be homogeneous tridymite. Some observations of its density are contained in the subjoined table under the heading "tridymite from quartz." A similar charge obtained by crystallizing the glass at 1200° (three days) also showed no residual glass under the microscope. Its density is given under the heading "tridymite from glass." A second table contains confirmatory measurements upon a second preparation heated to a slightly different temperature.

Tridymite (H_2O at 25° = 1).			
First preparation (1200°).		Second preparation (6 days at 1160°).	
From quartz.	From glass.	From quartz.[1]	From glass.
2.325	2.316	2.327	2.319
2.330	2.318	2.325	2.318
2.325	2.316		2.316
	2.319		
Mean, 2.326 (25°)	Mean, 2.317 (25°)	Mean, 2.326 (25°)	Mean, 2.318 (25°)

Whether the quartz had not completely changed to tridymite, or the glass was incompletely crystallized, or perhaps both, is of little moment. It is a very slow change and the agreement between the values obtained by the two methods is sufficiently

[1] This preparation was afterward found to contain some unchanged quartz.

good, when considered in the light of their identical optical properties, to establish the absolute identity of the tridymite formed from the glass and from the quartz crystals.

The Lime-Silica Series.—Having determined the properties of our two component minerals, we are prepared to enter upon the study of their relation to each other in mixtures of various proportions. It will be borne in mind that inasmuch as we found no proper melting-point for pure silica on account of the inertness (if we may so describe it) with which it resists molecular deorientation when heated, so compositions which are immediately adjacent to the silica end of the series may be expected to show the same property and to yield but little information from a direct application of the usual pyrometric methods. Similarly, pure calcium oxide and its immediate neighbors are well out of reach of accurate measurement by any existing pyrometers. But even without these important measurements, we have been able to obtain sufficient information in the more inaccessible portions of the curve to enable us to describe all the reactions involved with little probability of error. Inasmuch as lime is probably the most refractory mineral known, it will require no apology if we simply leave its thermal constants until greater perfection in pyrometric measurements shall have been attained.

Preliminary Orientation.—Given chemically pure and *well mixed* (by grinding and *repeated melting*) preparations, it is not a difficult matter to secure a preliminary survey of a field of this kind. The mineral wollastonite is known, and more than that, is known to possess a melting temperature lower than either lime or silica. There is, therefore, immediate reason for anticipating eutectic relations somewhere in the series. If wollastonite forms a eutectic with components on one or both sides of it, mixtures containing slightly more lime or slightly more silica than wollastonite will have lower melting temperatures than it. A simple and effective mode of preliminary procedure is therefore to take a tiny pinch of a number of the percentage mixtures adjacent to wollastonite, place them in order upon a narrow platinum ribbon which can be heated electrically to uniform brightness, and observe the order in which they melt. No temperature measurement is worth while; the information obtained can only serve for orientation and must be verified by more reliable pyrometric methods.

If a eutectic is present on either side of the compound, it will be the first to melt, and the compound last; the intermediate mixtures are not important. If the materials are not too viscous the melting will be sharp and the material will crystallize again on slow cooling. A few repetitions, or the introduction of intermediate compositions in doubtful cases, will usually enable a preliminary curve to be drawn in which the compounds and eutectics which are within reach will be correctly located. In fact, for many substances they can be very exactly located in this way; intermediate compositions, on the other hand, may be very misleading, depending upon the behavior of the eutectic present after the melting temperature of the latter has been passed.

Proceeding in this way, a eutectic will be readily located between silica and wollastonite at the composition 63 per cent. SiO_2, 37 per cent. CaO, and another on the other side of wollastonite at the composition 46 per cent. SiO_2, 54 per cent. CaO. We will allow the other component of this second eutectic to remain unidentified for the moment, as no stable lime-silica mineral richer in lime than wollastonite is known. If we continue our platinum ribbon experiment with continually increasing percentages of lime, we shall find that after one or two steps beyond this second eutectic the platinum ribbon will burn out without melting the little grains. In other words, the melting temperature of lime-silica mixtures richer in lime than 60 per cent. are all higher than that of platinum. To meet this difficulty, we substituted iridium for platinum ribbon, and proceeded as before laying out a whole series of compositions from 60 per cent. CaO on. We soon discovered a third and very sharp eutectic with the composition $67^1/_2$ per cent. CaO, $32^1/_2$ per cent. SiO_2, and a maximum indicating a probable compound at 65 per cent. CaO, 35 per cent. SiO_2, which corresponds to the anticipated orthosilicate. No other points were obtained up to 2100°.

Thus in a very short time and in this simple and expeditious way we were able to locate three eutectics (37, 54 and $67^1/_2$ per cent. CaO) and two compounds (48 and 65 per cent. CaO) between lime and silica, canvassing for the purpose practically all the compositions from pure lime to pure silica at intervals of 1 or $2^1/_2$ per cent. and all temperatures from 500° to 2100°. Beyond 75 per cent. lime and below 32.5 per cent. the method yields no informa-

tion for reasons which have been elaborated elsewhere. All the important determinations were verified by numerous repetitions.

If we now compare the compounds obtained by this preliminary investigation with those which we were led to anticipate from Boudouard's observations, as well as from the hypothetical silicic acids, we find that we have located two—the metasilicate and orthosilicate—and missed two—the åkermanite analogue ($4CaO.3SiO_2$) and the tricalcium silicate. The next step was therefore obviously to bring all our resources to bear upon these particular compositions in order definitely to ascertain whether such compounds can exist when the components are pure, and if so, under what conditions and with what properties. That we succeeded in reaching a positive conclusion upon this point is due in large measure to the skilful microscopic examinations by Mr. Fred Eugene Wright of this laboratory, of which a detailed record prepared by him will be found with the full text of this paper soon to be published.

The Åkermanite Analogue.—The åkermanite analogue ($4CaO.3SiO_2$) was first taken up and the neighboring concentrations investigated at intervals of 1 per cent. with the greatest care. A large charge of this particular composition was repeatedly melted and examined under the microscope but it failed to show homogeneous structure or any characteristic property of a compound. On the other hand, the pseudo-wollastonite and the orthosilicate appeared in the proportion appropriate to its place in the series. Furthermore, since the melting temperatures of these mixtures were within the reach of our platinum furnaces, and therefore of our most sensitive pyrometric measurements, we were able to hold the temperature constant at any desired point and then by rapid cooling (quenching in mercury) to fix any phase which might have been present and become unstable below that temperature. Here again we found that pseudo-wollastonite and the calcium orthosilicate were the only phases which could be separated from this or any mixture of the pure components in the neighborhood. It is our belief, therefore, that the åkermanite mineral cannot exist between the pure components and is only possible when other substances are present. This is further indicated by the fact that the metasilicate of calcium in the presence of magnesium oxide forms a solid

solution of which the limiting concentrations are relatively wide and which would easily account for the åkermanite mineral produced from the fusion of the three components.

The Orthosilicate of Calcium, Ca_2SiO_4 (65 per cent. CaO).[1]—It has long been known that the orthosilicate of calcium, although not found in nature, can be formed by the fusion of the pure components. The temperature of fusion is very high and the crystalline material obtained disintegrates spontaneously at the lower temperatures. The cause of the disintegration has not been carefully studied heretofore, and optical determinations of it are difficult, owing to the extreme fineness of the disintegrated product. Our investigation establishes the fact that the orthosilicate of calcium can exist in three polymorphic forms which we have designated as α, β and γ, in the order in which they form from fusion. The α-form is the only modification which is stable in contact with the melt. Its specific gravity is about 3.27, determined in methylene iodide solution upon fresh crystals. Its hardness is 5-6, Mohr's scale; crystal system, monoclinic.

Below 1410° the α- changes into the β-form, of which the density, 3.28 (measured by comparing the indices of refraction), is but little different from that of the α-modification. The substance was too unstable for determinations of the density to be made in the ordinary way. It crystallizes in the orthorhombic system. The inversion point between the α- and β-varieties is well marked and distinguishable over almost the entire range of compositions of which the orthosilicate is a component, as indicated in the diagram (Fig. 2, line *MN*). The inversion of β into γ occurs at about 675° with a large increase of volume, which at once explains the disintegration of the material. The temperature at which this inversion occurs is somewhat variable, and it is not readily reversible. It is much too slow a change to admit of pyrometric determination, but it is possible to locate it approximately by quenching the material from selected temperatures in the neighborhood of the inversion point. The usual procedure was to take a small portion of the disintegrated material, fold it tightly between thin strips of platinum and place these in the furnace. The temperature was then raised to any chosen value

[1] The metasilicate of calcium has been made the subject of a special paper by Allen, White and Wright (loc. cit.), and will not receive detailed consideration here.

and maintained constant for periods of time varying from six hours to three or four days. At temperatures far enough removed from the inversion point, the transition from one form into the other was fairly rapid, but as the temperature of inversion approaches, equilibrium is attained with increasing difficulty. After the furnace had remained at this constant temperature for a length of time, it was opened, the platinum strips containing the orthosilicate were removed, and quickly plunged into mercury. In this way, from temperatures just above the inversion point, it was possible to fix the β-form long enough to allow of its optical determination.

The disintegration on cooling appeared to depend considerably upon whether or not the α-form had first been allowed to change into the β-form. For example, if a small portion of the orthosilicate is fused before the oxyhydrogen blast and then plunged directly from the flame into mercury, the quenched material will usually be stable for a considerable time. If the flame is removed but a moment and the slightly cooled specimen plunged from white heat into mercury, disintegration is immediate. This phenomenon was further verified by fusing the material and dropping it into a furnace held at about 1200°. After a few moments the charge was then removed and quickly plunged into mercury. Treated in this way, all of α goes over into β, which in turn will disintegrate completely with little or no delay after reaching the $\beta \rightleftarrows \gamma$ inversion temperature. One will sometimes get the α-form by slow cooling, but never the β-form.

The γ-form of the orthosilicate crystallizes in the monoclinic system. Its density, determined in turpentine, by the pycnometer method, is

2.973
2.975

Mean, 2.974 (25°)

The difference in volume between the γ- and α- or β-forms is therefore nearly 10 per cent., and since the α- and particularly the β-form goes over into the γ at low temperatures with the greatest readiness, the disintegration of the fused orthosilicate is readily explained.

Neighboring mixtures containing the orthosilicate as a component disintegrate beginning with compositions containing only 51 per cent. of lime. The disintegration of this preparation

is, however, very slow, and usually does not take place at all unless the mixture has been held for some time at a relatively high temperature. The 54 per cent. mixture can also be readily obtained without disintegration, but with more than 54 per cent. of lime, disintegration always occurs under the ordinary conditions of preparation.

If the orthosilicate be heated to temperatures only slightly above *QR* (Fig. 2) so as to produce the β-form without sintering, disintegration does not appear on cooling for the reason that the change in volume is not apparent in the powdered material. If the charge be heated to about 1400°, or above 1410° where the α-modification appears, it sinters tightly together and the disintegration phenomenon is again observed. Charges sintered together at 1400° to 1500° and held continuously at any temperature above *QR* do not disintegrate so long as this temperature is maintained, but as soon as the temperature drops below *QR*, disintegration recurs, but not at a constant temperature nor at any characteristic rate, the change being very dependent upon the conditions obtaining at the time.

The orthosilicate is easily attacked by water, giving an alkaline reaction, even when the water is cold, while with boiling water it is possible to wash out as much as 10 per cent. of lime. This probably accounts for the absence of this mineral in nature. Ammonium chloride solution even when cold decomposes all the mixtures of lime and silica.

The Tricalcium Silicate,[1] $3CaO,SiO_2$.—This silicate owes its supposed existence mainly to those investigators who have found it necessary to postulate such a compound in order to explain the constitution of Portland cement. So far as the literature shows, no one has ever isolated and described a pure and homogeneous compound of this composition or defined its properties.[2] Many and varied attempts to make it have uniformly resulted in mixtures in which poor optical properties have made the conclusions insufficiently positive.[3]

[1] In the literature of the cement industry the hypothetical compound, $3CaO,SiO_2$, is almost universally referred to as the "tricalcic silicate." The substitution of "tricalcium silicate" in conformity with common chemical usage will of course cause no confusion.

[2] It is sometimes described as "nearly homogeneous."

[3] A moment's consideration should suggest that there is no real necessity for assuming the existence of the tricalcium silicate in order to explain

We began the investigation of this composition by fusing the components in the proper proportions and examining the fused product microscopically as others had done. Most previous investigators, however, appear to have depended for microscopic evidence upon the ordinary optical figures and interference colors. Now, it so happens that this mixture when fused crystallizes in an extremely fine structure in which the interference colors are quite different from those of the orthosilicate to be sure, but this is merely the result of the fine state of division and the overlapping of the crystals, and not to another compound. If one examines any of the compositions in which the tricalcium silicate might be expected to figure, using the very sensitive index of refraction as a test of homogeneity, he will find that in every preparation containing more lime than 65 per cent. (orthosilicate composition), there is an excess of free lime which can be positively identified. We have fused the tricalcium silicate composition, cooled it rapidly and slowly in various ways without once failing to find free lime present in quantity. Through the kindness of Dr. Clifford Richardson, we were also given an opportunity to examine some of the tricalcium silicate prepared and described by him, and while its ordinary appearance under the microscope differed from that of the orthosilicate, a study of the index of refraction showed the supposed tricalcium silicate to be a mixture of the orthosilicate with free lime. Having failed to obtain a single tricalcium silicate which did not contain free lime, and because every specimen which we examined, including many which had been prepared by others, also showed the orthosilicate to be present, we were forced to conclude that the tricalcium silicate has no real existence. We also tried fusing the tricalcium silicate composition with a flux, but the product was always the orthosilicate of calcium.

the nature of Portland cement. It is a system of at least three components with a great number of possibilities. The real difficulty appears to have been that crystallized lime is relatively inert and does not readily give the reactions common to ordinary lime, consequently the tests which were thought to demonstrate the absence of free lime in these preparations have proved very misleading. For example, we have found that crystals of lime are but very slowly attacked by water (see p. 1094). Another argument which is freely offered—that there can be no free lime present "because if free lime is added the cement dusts spontaneously," is obvious fallacy. Free lime does not cause the dusting, and if it did the fact that the *addition* of free lime caused dusting would be no proof that none was present.

Although we are anticipating pyrometric studies which follow, a single glance at our diagram (Fig. 2) will show that we have found and measured the $\beta \rightleftarrows \alpha$-inversion of the orthosilicate in all the compositions up to 90 per cent. lime which we could never have done with a tricalcium silicate intervening unless the tricalcium silicate be assumed to possess an identical inversion—which would be a rare coincidence. We have therefore complete optical and pyrometric evidence of the persistence of the orthosilicate throughout the supposed tricalcium silicate region, and no compound of tricalcium silicate composition can exist there.

By way of completing the search for hypothetical compounds, we also examined compositions corresponding to the trisilicic acid, but found that the mixtures of lime and silica from which the salt of this acid might be expected to crystallize did not give any new phases. These mixtures showed well developed pseudo-wollastonite with the tridymite eutectic, and neither rapid cooling nor crystallization of the glass at low temperatures gave any indication whatsoever of the hypothetical compound.

The Temperature Constants.—We have now definitely located the compounds of lime and silica which can exist between the pure components together with the eutectics which they form. It only remains to study their thermal properties somewhat more consistently by accurate pyrometric apparatus. It was not found possible to determine the presence of the eutectic (line *HBI*, Fig. 2) in the 10 and 20 per cent. compositions, for reasons which will have become sufficiently clear already, but the microscopic evidence shows the tridymite to be normal, whether it forms from pure silica or in the presence of lime, so that the eutectic must extend over to the silica axis. From 30 per cent. on there was no difficulty in observing it pyrometrically. Mean values of the observations obtained are included in Table I.

TABLE I.

(Line *HI*, Fig. 2.)

	Eutectic.	Tridymite—pseudo-wollastonite.			
Percentage of CaO	30	32	35	40	45
Eutectic melts.....	1420°	1418°	1418°	1421°	1413°

The liquidus *AB* (Fig. 2) has been drawn as a dotted line. The value assumed for the melting temperature of silica is based upon considerations which have been elaborated elsewhere (p. 1095). It requires no further comment except perhaps to call

attention to the fact that it is much lower than the temperature usually assigned to it. As the mixtures grow richer in lime, the melting of the excess of silica seems to be considerably facilitated, but there are no points sufficiently sharp to serve any purpose as quantitative determinations until we reach the composition 30 per cent. CaO, 70 per cent. SiO_2. The microscopic evidence is, however, both satisfactory and sufficient as to the nature and continuity of the curve.

Along the branch *BC* (Fig. 2) of the liquidus, the pseudo-wollastonite is the solid phase. It crystallizes from these mixtures in laths between which an extremely fine-grained, almost submicroscopic eutectic appears.

It may be remarked in passing that the "eutectic structure" in minerals is by no means so characteristic as in the case of the alloys. Owing to the great viscosity of these melts and consequent slowness of diffusion, it is evident that there is no opportunity for the formation of the characteristic grain structure which we have come to associate with the eutectics of the alloys. This almost complete absence of diffusion in silicate melts makes it necessary to proceed with great caution in applying to minerals the methods which are easily and effectively applied to the alloys. For example, in alloys it is possible to crystallize out a portion of the solid phase, then to separate the mother-liquor and by analysis of the two to determine the composition of the solid phase. In the case of mineral mixtures, the segregation of the eutectic is, for laboratory experiments at least, very indefinite. We have repeatedly examined different regions of a charge in which the eutectic was known to separate, in the hope of finding it segregated towards the middle of the charge, as commonly happens with alloys, but in no case were we able to detect more of the eutectic in one part of the charge than in another. It is usually finely divided and intimately mixed with the primary crystals.

The properties of the pseudo-wollastonite which separates along the branch *BC* are not quite identical with those of the compound when prepared pure, from which it is evident that a certain amount of silica must be taken up by it in solid solution. The amount thus held in solution is certainly less than 2 per cent., but its exact determination microscopically is very difficult indeed. Furthermore, this pseudo-wollastonite when changed to

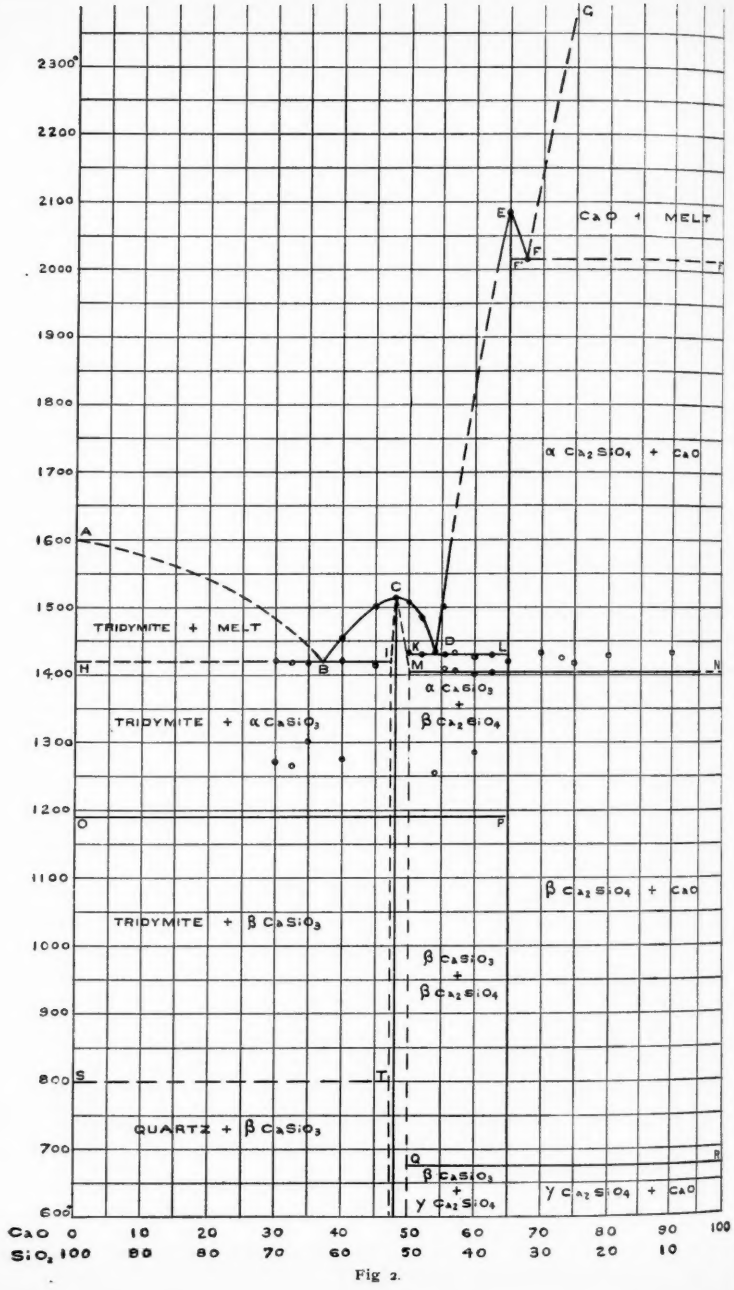
2300°
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
C
E
F
CaO + MELT
α Ca2SiO4 + CaO
A
C
TRIDYMITE + MELT
B
K
D
L
H
M
N
α CaSiO3
+
β Ca2SiO4
TRIDYMITE + α CaSiO3
O
P
β Ca2SiO4 + CaO
TRIDYMITE + β CaSiO3
β CaSiO3
+
β Ca2SiO4
S
T
Q
R
QUARTZ + β CaSiO3
β CaSiO3
+
γ Ca2SiO4
γ Ca2SiO4 + CaO
CaO 0 10 20 30 40 50 60 70 80 90 100
SiO2 100 90 80 70 60 50 40 30 20 10

Fig 2.

wollastonite still shows a slightly different optical character from the pure material, showing that the solid solution apparently continues after the inversion. For brevity, the pseudo-wollastonite has been designated α-$CaSiO_3$, and wollastonite β-$CaSiO_3$, in (Fig. 2). The branch of the liquidus *CD* was readily determined, as well as the beginning of the branch *DE*. It was not possible, however, to follow the branch *DE* beyond 57 per cent. owing to the steepness of the curve, which rapidly carries it out of the range of the accurate thermoelectric methods.

Mean values of the observations along the curve of melting-points are continued in Table II.

TABLE II.

(Curve *A B C D E F G*, Fig. 2.)

Curve of Melting-points.

Percentage of CaO	40.0	45.0	48.2	50.0	52	54	55.5	65	67.5
Component in excess melts	1453°	1500°	1512°[1]	1508°	1484°	1433°	1503°	2080°[2]	2015°[2]

The eutectic *KL* (pseudo-wollastonite + α-calcium orthosilicate), Table III, was found in all compositions containing more than 50 per cent. and less than 65 per cent. of lime. No trace of it could be detected in the 65 per cent. composition, though diligent search was made for it. A great many determinations were made of it of which only the mean values are given in Table III.

TABLE III.

(Line *KL*, Fig. 2.)

Eutectic. Pseudo-wollastonite + α-Calcium Orthosilicate.

Percentage of CaO	50	52	54	55.5	57	60	62.5
Eutectic melts	1432°	1430°	1433°	1429°	1431°	1426°	1429°

The properties of the metasilicate separating along *CD* are also slightly different from those of the pure pseudo-wollastonite, and up to 50 per cent. the mixture appears homogeneous, so that the metasilicate probably takes up about 1 per cent. of orthosilicate in solid solution.

The melting-point of the orthosilicate determined in the iridium furnace was found to be

[1] Determined by Allen and White, Loc. cit.

[2] Determined with the Holborn-Kurlbaum optical pyrometer in the iridium furnace.

2077°
2085°
2083°

Mean, 2082°

Another charge observed at 2035° was found to be entirely unmelted. Optical methods of temperature measurement are not competent to determine the melting temperature of the orthosilicate in the presence of the eutectic for reasons already explained (p. 1091), but the eutectic or the compound is readily measured by itself once the composition has been determined. Applying the method to the $67^1/_2$ per cent. mixture, therefore, it was found to melt very sharply at 2015°. Neither the orthosilicate nor the 70 per cent. lime composition showed any trace of fusion at this temperature. Since the microscopic properties of the orthosilicate remain unchanged in the presence of an excess of lime or of silica, it follows that the orthosilicate does not form solid solutions with either lime or silica. Both eutectics will therefore continue up to the orthosilicate. Above the lime-orthosilicate eutectic the pyrometer affords no further information regarding the melting-point curve.

The line *MN* (Fig. 2) represents the temperature at which the inversion of β-orthosilicate occurs. It will be noted that the inversion is frequently delayed by superheating, especially in the region remote from the eutectic, but it was always possible to show by quenching the material from above and below these temperatures that the variation is merely due to the inevitable lag of the reaction. Between 50 and 65 per cent. of lime, the two heat changes at *MN* and *KL* lie so close together that it was very difficult to separate them. The pyrometer shows two points plainly but each is somewhat displaced by the other. We were able, however, to distinguish them beyond possibility of confusion by holding the furnace constant at 1425° and quenching the charge in water. These conditions yield α-orthosilicate + pseudo-wollastonite, while if the temperature is held at 1390-1400°, β-orthosilicate + pseudo-wollastonite results. The inversion temperatures are contained in Table IV. Mean values are, of course, without significance.

TABLE IV.

Inversion. β-Orthosilicate to α-Orthosilicate.

Percentage CaO.	55.5	57.0	60.0	62.5	65.0	70	73	75	80	90
Inversion temp.	1407°	1395°	1404°	1396°	1426°	1409°	1426°	1415°	1407°	1438°
	1414	1412	1411	1397	1421	1405	1425	1421	1429	1432
	1403	1419	1411	1405	1415	1412			1432	1433
	1411	1415	1398	1398	1414				1425	
		1406	1402	1408	1412					
		1406	1404	1407	1413					
		1404	1405	1401	1417					
			1388		1423					
					1411					

The scattered points lying below 1300° (Fig. 2) occur only in the compositions in which the metasilicate is present, and correspond, as a microscopic examination at once shows, to the change from wollastonite to the pseudo-hexagonal form. With falling temperature, the points occur very much lower or are lost, since the inversion does not occur quite as readily on cooling. Allen and White observed that this inversion could be brought about only with great difficulty with the pure metasilicate, but in the presence of an excess of either lime or silica, we found it to occur with comparative readiness (Table V) in many compositions. The line QR is the temperature at which the reaction β into α takes place. As observed in the discussion of the properties of the orthosilicate, this reaction does not occur promptly, but is liable to very serious superheating or undercooling.

TABLE V.

Inversion. β-Metasilicate to α-Metasilicate.

Percentage CaO.	30	32.5	35	40	45	57
Temperature of inversion..	1273°	1274°	1257°	1288°	1254°	1286°
		1263	1399	1266		
			1323			
			1328			

SUMMARY.

There are only two definite compounds of lime and silica capable of existing in contact with the melt. These two compounds are:

(1) The pseudo-hexagonal metasilicate melting at 1512° and inverting into wollastonite at about 1200°. The metasilicate is able to take up a small amount of either lime or silica in solid solution.

(2) The orthosilicate of calcium which melts at 2080° possesses three polymorphic forms:

The α-form, which crystallizes in the monoclinic system, has a density of 3.27 and a hardness of between 5 and 6.

The β-modification crystallizes in the orthorhombic system and has a density of 3.28.

The γ-modification has a density of 2.97, and also crystallizes in the monoclinic system. The disintegration or "dusting" of the orthosilicate and of all lime mixtures above 51 per cent. lime is due to the 10 per cent. volume change accompanying the $\beta \rightleftarrows \alpha$ inversion.

The inversion point α to β occurs at 1410°, β to γ at 675°.

There are three eutectics in the series: Tridymite + the metasilicate at 37 per cent. lime, 1417°; the metasilicate + orthosilicate at 54 per cent. of lime, 1430°; and orthosilicate + lime at $67\frac{1}{2}$ per cent. of lime, 2015°.

The orthosilicate is readily attacked by water, which dissolves out the lime in large quantities. This is probably the reason why it is not found as a natural mineral.

The density of fused lime is 3.32; its hardness 3+. It fuses in the electric arc but its fusion temperature is not accurately measurable. Lime crystallizes in the isometric system and possesses no polymorphic forms.

Silica begins to melt at about 1600° to an extremely viscous liquid, so that an exact melting-point cannot be determined. It has been shown that for all temperatures above 1000° pure quartz changes into tridymite, and pure quartz glass crystallizes as tridymite; so that above this temperature tridymite is unquestionably the stable phase. In the presence of fused chlorides quartz glass crystallizes as quartz at temperatures up to 760° and as tridymite above 800°, crystalline quartz inverts to tridymite above 800° and tridymite goes back to quartz at 750°. The inversion temperature is therefore about 800°, and the change is enantiotropic. The density of pure tridymite was found to be 2.318, and that of quartz glass 2.213. The pure natural quartz used had a density of 2.654, the artificial crystals of 2.650.

Neither the salt of the trisilicic acid, $2CaO, 3SiO_2$, the åkermanite analogue, $4CaO, 3SiO_2$, nor the tricalcium silicate, $3CaO, SiO_2$, can exist in the two-component system.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 127.]

PLATINUM SILVER ALLOYS.

BY JOHN F. THOMPSON AND EDMUND H. MILLER.

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THE solubility of platinum, when alloyed with silver in nitric acid, may be considered one of the historical facts in the history of the metal, as its announcement by the Graf von Sickingen[1] in 1782, came only forty-six years after the discovery of the element platinum, thus placing it among the earliest known chemical properties. The reasons for and quantitative relations of this solubility have, however, remained unexplained up to the present day, in spite of the numerous attempts on the part of various experimenters. The results of these authors have been conflicting in the extreme, and not only have the later investigators failed to confirm the earlier, but their results in themselves offer no explanation as to the cause of the anomalies. Thus, Clemens Winkler,[2] working with alloys containing percentages of platinum varying from 1 per cent. to 10 per cent., found that the strength of acid used was of small importance, while the weight of residue left, assumed by him to be platinum, was on the average about 66 per cent. of the weight of the original alloy. This percentage varied somewhat irregularly with the strength of acid and percentage of platinum in the alloy, and, in general, decreased with the platinum content of the alloy. John Spiller,[3] on the other hand, investigating alloys of the same range of platinum content, found acid of 1.42 specific gravity to be the best solvent, but records that, even under the most favorable conditions, only 0.75 to 1.25 per cent. of the platinum could be dissolved along with the silver. H. Rose[4] found that, at the most, 10 per cent. went into solution with the silver. N. W. Perry,[5] in a description of an assay method, states that after removing the base metal by cupellation, the platinum could be dissolved completely along with the silver, provided the platinum were alloyed with at least

[1] Muspratt, 4th Ed., 7, p. 255.
[2] Z. anal. Chem. 1874, p. 368.
[3] Pr. Chem. Soc. 13, 118 (1897).
[4] Rose: Handb. Analyt. Chem., 6th Ed., 2, 226.
[5] Eng. Min. J. January, 1879.

twelve times its weight of silver. E. H. Miller,[1] in a comparison of the various wet and assay methods for the determination of platinum, repeated Perry's work and found that, even with a platinum-silver ratio of twenty-seven to one, some platinum remained undissolved. The results in this case were, however, complicated by the presence of iridium and gold in the material experimented on. Later, von den Ropp,[2] in a series of experiments on alloys containing up to 30 per cent. of platinum, found that alloys containing not more than 23 per cent. of platinum could be brought completely into solution by treating them with nitric acid, washing the residue free from nitric acid with water and then treating with hydrochloric acid. Besides this new and positive fact brought out by von den Ropp's work, he also investigated to some extent the black residue left on treating the alloy with nitric acid, and tried the solvent effects of hydrochloric acid, sulphurous acid and ammonia in the order named, the treatment with each reagent being followed with a complete washing of the residue with water, the solutions and wash-waters being kept separate. In this way von den Ropp obtained a series of solutions or colloidal solutions. The cause of the solution of parts of the residue in this way, or the composition of the parts dissolved were, however, not investigated. Finally Krug,[3] in an investigation of the alloys of platinum and copper, found that the residue left on dissolving the alloys in nitric acid, and which he, as well as Winkler and von den Ropp, found to be explosive when heated with organic materials, *i. e.*, filter-paper, consisted of a nitrate. Krug explains the solubility found by von den Ropp (see above), as being merely a reaction of the hydrochloric acid used against this compound giving chlorine which dissolved the platinum. He also advanced the idea that the solutions obtained by von den Ropp with various reagents were simply forms of colloidal platinum. This latter idea will be discussed later in connection with some further solubility experiments. Beside these investigations of the solubilities of the binary alloys of platinum, several papers have been published dealing with experiments on the parting of ternary and even quaternary alloys containing platinum and silver. The results

[1] School of Mines Quarterly, 17, 26 (1895).
[2] Berlin Dissertation, 1900.
[3] Leipzig Dissertation, 1903.

have in most cases been unsatisfactory, as the problem which, in the case of binary alloys, presented wide inconsistencies in similar work done by different investigators, has in the case of ternary and quaternary alloys become so complicated that it is impossible to decide what variable is responsible for any given set of results. The papers dealing with this phase of the subject will, therefore, not be reviewed in full, but will only be referred to when their results have some direct connection with either our experimental results or conclusions. In a foot-note, reference will be found to some of the more important or recent articles.[1]

As may be seen from the foregoing review, neither the primary fact of why platinum dissolves when alloyed with silver, or the secondary facts as to the quantitative relations of this solution have ever been firmly established. Chemical investigation alone would be enough to settle the latter. It is difficult to see, however, how strictly chemical methods could ever solve the first problem or give the basis on which the results of solution tests could be satisfactorily interpreted. The following investigation was therefore started with the idea of studying the physical properties of the platinum silver alloys and using the results so obtained in the interpretation of a series of solubility tests run in comparison with those of previous investigators.

The physical properties chosen for investigation were the melting-points and cooling curves, microstructure, specific gravity and electrical conductivity of the different alloys. These, it was felt, would give a sufficiently wide range of properties, so that reliance could be placed on a confirmation of the results of one series by those of another. A careful survey of the literature was made before beginning this study, with very little result. In this connection the assistance obtained from the excellent bibliographies of Howe[2] and Sack[3] should be acknowledged. On cooling curves the only quantitative data which could be found were given by a partial curve published by Heycock and Neville.[4] These

[1] Carmichael: J. Chem. Ind. **22**, 1324 (1903); Sharwood: Ibid. **23**, 412 (1904); Richards: Analyst, **27**, 265 (1902); Neveu: Ann. Chim. anal. appl. **8**, 161; Hollard and Burtiaux: Ibid. **9**, 287.

[2] Bibliography of the Metals of the Platinum Group. Smithsonian Misc. Collections, Vol. 38, No. 1084.

[3] Bibliographie der Metallegierung, Z. anorg. Chem. **35**, 249 (1903).

[4] Phil. Trans. **189**, A. 25 (1897).

authors investigated alloys containing up to 2 atomic per cent.[1] of platinum (3.55 per cent. by weight) and found that the freezing-point curve rose sharply away from the freezing-point of silver, the alloy containing 2 atomic per cent. of platinum freezing at 990°. Matthiesen,[2] in an account of some experiments on certain platinum silver alloys, refers to the 33 per cent. alloy being at a critical point in electrical resistance. Beyond these references all data that could be found were either inapplicable to the present work or too vague as to percentages of platinum, etc., to be of any use.

EXPERIMENTAL.

The first step was the purification of the materials used and the preparation of alloys of known composition and proved homogeneity, the last two points being questions which had been neglected by previous investigators.

Purification of Materials.—The platinum used was a supposedly chemically pure foil from a foreign maker, but was shown by qualitative analysis, using the method of Mylius and Dietz,[3] to contain iridium. It was, therefore, freed from this by the following purification method.[4] This consisted in dissolving the impure platinum in aqua regia and freeing from nitric acid by repeated evaporations with hydrochloric acid. This hydrochloric acid solution, containing both of the elements in their highest state of oxidation, was then taken to dryness and heated on an electric hot plate for several hours at a temperature of 125°. It was then taken up with hydrochloric acid and water and precipitated by the addition of ammonium chloride and alcohol. The iridium, which had been reduced by the heating to a lower chloride, not being precipitated by the ammonium chloride, passed into the filtrate along with some of the platinum, also reduced. The

[1] Atomic per cent. may be calculated as follows, for any series of binary alloys A—B:

$$\text{Atomic } \%\ \text{A} = 100 \frac{\dfrac{\text{weight A}}{\text{atomic weight A}}}{\dfrac{\text{weight A}}{\text{atomic weight A}} + \dfrac{\text{weight B}}{\text{atomic weight B}}}$$

Weight A and B being taken as parts in 100.

Grube: Z. anorg. Chem. **44**, 122 (1905).

[2] J. Chem. Soc. **20**, 201 (1867).

[3] Ber. 1898, 3137.

[4] Encyclopedia Britt. 9th Ed., **19**, 201.

ammonium chlorplatinate was then dried and tested for purity by spreading it out on a glazed paper and examining portions selected from different parts thoroughly under a microscope (80 diameters). In no case, although eight separate portions were examined from each lot, could any salt be detected except the yellow crystals of ammonium chlorplatinate. This salt was then converted to metallic platinum by ignition and washed successively with hydrochloric acid, water, nitric acid and water. The sponge so obtained was either used as such or melted with the oxyhydrogen blowpipe and rolled out into foil.

The silver was guaranteed by a reliable maker to be at least 999 fine, and was used without further purification. As will be shown later, the thermal analysis enabled us to make a check on the purity of the silver by means of a determination of its melting-point.

Preparation of Alloys.—To be used for a preliminary survey of the field, five alloys, weighing 10 grams each, were made, containing approximately 10, 20, 30, 40 and 50 per cent. of platinum. The method of preparation was the same throughout, except that the 40 and 50 per cent. alloys were made from the platinum sponge on account of the greater ease of alloying compared with the foil from which the others were made. In all cases, the silver was first melted in a No. 1 French clay crucible in a small Fletcher furnace. After it was thoroughly melted, the platinum was added piece by piece, if used as foil, or wrapped in an ashless filter-paper, when the sponge was employed. Heating was continued for about five minutes, when the crucible was withdrawn from the furnace and shaken violently until the melt solidified. It was then replaced, and this treatment, melting, holding melted for two to three minutes and then removing and shaking until the button solidified, repeated several times. The crucible was then removed from the furnace and the button allowed to solidify and removed from the crucible. It was then replaced in the crucible in an inverted position and the previous treatment repeated, so that any pieces of platinum which might have sunk to the bottom of the button and so escaped the effect of the several shakings, would come more intimately in contact with the melt. After several such heatings the button was allowed to cool and was cut in half vertically. One of the faces so exposed was then polished and examined with a metallographic microscope for any

pieces of unalloyed platinum. If any such were found, the alloy was remelted and the previous treatment repeated until no platinum could be found unalloyed on careful microscopic examination. In cutting the alloys for microscopic examination, considerable difference in their hardness was noted, which will be discussed later in connection with their other physical properties. Before starting the preparation of the alloys, it was feared that the furnace used would not give sufficient heat to melt the alloys of higher platinum content. This fear was, however, without foundation, for using a false top, so that a higher rate of combustion could be used, and also a supplementary blast-lamp of the Waller type, blowing in at the same tuyere hole as the regular blast, it was found that temperatures of 1450° could be reached in the crucible.

Thermal Analysis.—The freezing-points and cooling curves of the alloys were next taken in the Fletcher furnace, the No. 1 French clay crucible holding the alloy being surrounded by a larger crucible to decrease the rate of cooling. The method used was that of direct observation, using a Siemens and Halske galvanometer and a platinum-platinum 10 per cent. iridium thermocouple. The wires for this couple were made with great care in order to insure perfect homogeneity. In fact the platinum iridium was melted and shotted in water four times before the final ingot was cast. The wires were next thoroughly annealed by means of electrical "glowing" to remove any strains from the wire-drawing and were then investigated and found to be thermoelectrically homogeneous. This was done by taking each wire and connecting one end to each of the terminals of the galvanometer by means of two copper wires, the ends of the platinum or platinum alloy wire being contained in an ordinary cold junction bottle. By heating successive places on the wire, it could be shown that the wire itself was homogeneous throughout, or at least that there were no sudden variations in composition. That the wires were not of progressively changing composition was shown by making each end of the wire successively the hot junction and comparing with a second couple. The maximum error found in this way amounted to 2°. This precaution of testing for thermoelectric homogeneity is essential in case it is not desired to make use of more than one junction in a series of determinations of a single point and especially in a Fletcher furnace, where

the length of couple heated can not be easily varied to suit the convenience of the operator. The wires of the couple having been annealed and shown to be homogeneous, the couple was next standardized against the boiling-point of pure sulphur, using a Barus boiling-point tube, and against the freezing-point of Kahlbaum's copper. The sulphur used was in the form of crystals from carbon disulphide and was boiled thoroughly to free from any carbon disulphide, either of crystallization or mechanically held. Its boiling-point was taken at 444°.[1] The freezing-point of the copper was taken as 1084°[2] and the determinations were made under a layer of charcoal, the copper being melted under this layer, held melted for some time and also poled with a stick to insure complete reduction. From these points the curve of the couple was calculated, using Holman's logarithmic formula.[3] As a check on the accuracy of this curve, the melting-point of Kahlbaum's antimony was next determined, and in all cases fell within a limit of error of 3° from the temperature of 630° which was taken as the true melting-point.[4] A further check on the accuracy of the standardizing was obtained by the determination of the freezing-point of silver, which was determined in a graphite crucible under a layer of charcoal. This also in every case fell within the 3° limit and formed a very good check on the purity of the silver used in the preparation of the alloys. The melting-point of pure silver free from oxygen was taken as 961°.[5] In taking the melting-points and cooling curves of the alloys themselves it was not possible to use a charcoal cover, as the disturbing influence of oxygen was preferable to any risk of the platinum forming a carbide or taking carbon into solution. It is probable that this influence was of importance only in the alloys of lower platinum content, as with the higher alloys no noticeable spirting took place. Several experimental difficulties arose in these freezing-point and cooling-curve determinations, due largely to the use of such small amounts of alloys as to make the evolution of heat at any one temperature very small. In all

[1] LeChatelier and Boudouard's "High Temperature Measurements," 2nd Eng. Ed., 296.

[2] Holborn and Day: Am. J. Sci. 11, 145 (1901); 8, 165 (1899).

[3] Holman: Pr. Am. Acad. 31, 234.

[4] Day and Allen: Phys. Rev., Sept., 1904.

[5] Holborn and Day: Am. J. Sci. 11, 145 (1901); 8, 165 (1899).

cases the couple cover was clamped in place so that the end of the couple would come as near as possible to the center of the melt.

Electrical Resistance, Specific Gravity and Ductility.—After the thermal analysis had been finished, the alloys were remelted in crucibles of such a shape that the resulting buttons were in the form of cylinders of approximately 9 mm. diameter. A section was cut from the bottom of each button and reserved for microscopic examination while the remainder of the button was rolled out into tape. The rolling out of the alloys was kindly done for me by Mr. Cohn of the platinum-refining firm of Belais & Cohn, of New York City. From this tape a piece of uniform cross-section was cut out, which was thoroughly annealed and used for the measurement of the electrical resistance. This measurement was done for me on a Wolff bridge, by Mr. A. H. Nelson, of the Department of Physics, to whom I wish to express my thanks.

ELECTRICAL RESISTANCE EXPRESSED IN OHMS PER SQUARE MILLIMETER PER METER.

0.0	per cent.	platinum	}	0.0217
100.0	"	" silver	}	
10.39	"	" platinum	.....	0.0918
20.59	"	" "	.....	0.1814
31.46	"	" "	.....	0.2914
37.89	"	" "	.....	0.3110
57.05	"	" "	.....	not determined

The alloys were then cut into small pieces for further investigation by means of a large pair of shears. In this connection the very interesting qualitative fact may be noticed of the very marked change in ductility and in actual hardness which accompanied the increasing platinum content. This had already been noticed when cutting up the alloys for the different microscopic examinations and the same observations were repeated when the alloys were rolled. Thus the pure silver could be cut and rolled in the manner to be expected from its well-known soft and ductile nature; that is, the hack saw was not appreciably dulled by cutting a button and, in rolling, several passes could be made each time before the button had to be annealed. The 10 and 20 per cent. buttons were very much like it in both of these properties. With the increase of the platinum content up to 30 per cent., however, a marked change was noted in the behavior of the buttons. In cutting, the buttons were much harder and this hardness in-

creased rapidly with the increasing platinum content. Thus, while the 31 per cent. button cut with more difficulty than the lower ones, but was still comparatively soft, the 57 per cent. alloy was, on the other hand, so hard that several saws were broken each time a button had to be cut. This property was still more marked in the case of the rolling, and was shown by the increasing frequency with which the alloys had to be annealed in order to get them to go through the rolls without cracking. The limit of this was reached with the 57 per cent. alloy, which would stand almost no reduction and cracked so badly on the first pass that further rolling and, therefore, the measurement of its electrical resistance, had to be abandoned. Since the object of the investigation was to study simply those properties which would tend to throw some light on the chemical behavior, the question of changes in hardness was followed no further and no attempt was made to check these very rough qualitative results by means of sclerometer measurements.

The alloys having been cut up into small pieces, their specific gravity was measured, using a weighing-bottle, as compared to that of water at 4°, with the following results:

Pure silver	10.61
10.39 per cent. platinum	11.17
20.59 " " "	11.80
31.46 " " "	12.57
37.89 " " "	13.19
57.05 " " "	14.25

Analysis.—In order that the results on the various alloys might be referred to alloys of known composition, the alloys were analyzed by means of the standard parting with sulphuric acid. From the table of results, given below, the necessity of this step is plainly shown and gives some explanation as to the cause of the anomalous results of some previous investigators, who in no case had any further knowledge of the composition of their alloys than that gained from the proportions used in making them up. As in making our alloys the quantities of the metals were weighed exactly for making alloys of 10, 20, 30, 40 and 50 per cent. of platinum, the magnitude of the error even when working carefully in crucibles may be observed, and shows that the composition of the alloys made on charcoal before a blowpipe can only be a matter of conjecture, no matter how carefully the materials

may have been weighed. As carried out, the parting differed somewhat in detail from that generally described. In fact the methods as given in most descriptions of the process could not fail to give inaccurate results. One description provides for parting 300 mg. of the alloy for fifteen minutes over a Bunsen burner in a parting flask with 10 cc. of pure concentrated sulphuric acid. The acid was then allowed to cool and decanted into a beaker containing distilled water. The residue was treated as before with 5 cc. of strong sulphuric acid, decanted into the same beaker, and washed till free from acid, adding the washings to the silver sulphate solution. The platinum is then transferred to a small crucible by inverting, dried in an air-bath and weighed. By this means the author, working on an alloy containing over 33 per cent. of platinum, obtained results differing only by 0.1 per cent. on four separate determinations, and states that the platinum was tested for silver, but was found to contain only a minute trace. He further states that the silver may be estimated in the filtrate by the thiocyanate method, or, as in his work, by difference.

In attempting to follow out this method it was found that, even with closely agreeing duplicates, entirely erroneous results were obtained, for the following reasons: (1) In decanting the sulphuric acid solution from the residue platinum passed over with the solution. This platinum was in either a very finely divided or colloidal state, giving a dark color to the solution. The state of division was so fine, that not even by allowing the beaker containing the decanted filtrate to stand on a piece of white paper could any particles be seen as such. That they were present, however, is shown by the fact of their separating, if the solution was allowed to stand over night. And further, the fact that this separation on standing was due to particles already contained in the solution, and not to colloidal platinum or to a precipitate formed by some unnoticed reaction during standing, was shown by taking two portions of the same alloy and parting in the same way with sulphuric acid. One of these solutions was decanted and allowed to stand over night, and in the morning a fine black precipitate was found on the bottom of the containing beaker. The second solution was diluted and filtered, when a black precipitate was found on the filter-paper, and the filtrate on standing threw down no further precipitate. (2) The platinum

residue left, always contained some silver. This was less in amount with the lower platinum alloys, but was always a weighable quantity, and in the higher alloys became of very considerable importance. The use of the thiocyanate method for determining the silver in the filtrate was tried, but was not successful, in the presence of the large amounts of sulphuric acid from the solution of the alloy. By precipitating the silver from this acid solution with aluminium foil, dissolving in nitric acid and titrating, better results could be obtained, but the duplicates were not satisfactory.

The method finally adopted was as follows: 300 mg. of the alloy were taken and heated for fifteen minutes in a beaker with 10 cc. of concentrated sulphuric acid on an asbestos pad over a Bunsen burner. This solution was then decanted into a beaker and the alloy broken up by poking the pieces with a stirring rod, and then re-treated for fifteen minutes with 5 cc. more of concentrated sulphuric acid. The solutions were then combined, diluted, filtered through an ashless paper, and washed till entirely free from silver salts. The residue on the paper was then ignited in a porcelain crucible and weighed. This residue was then dissolved in aqua regia and by several treatments with nitric acid, followed by taking the solution gently down almost to dryness most of the free acid was removed, and the free acid that remained was nitric and not hydrochloric. The solution was then diluted somewhat, and the silver precipitated by the addition of common salt in the usual way. The precipitate obtained in this manner was of a reddish yellow color, apparently due to admixed silver chlorplatinate. This precipitate was filtered and washed free from chlorides. It was then dissolved through the paper with dilute ammonia and reprecipitated in the filtrate with nitric acid and a drop or two of hydrochloric acid. It was filtered and weighed in the regular way. It was found that this solution of the impure silver chloride and reprecipitation gave a perfectly white precipitate, while the platinum passed into the filtrate. The strong sulphuric acid solution containing the silver was treated in one of two ways: (1) By diluting to about 900 cc., partly neutralizing and precipitating the silver as sulphide at a temperature of about 90°, filtering, dissolving the sulphide in nitric acid and reprecipitating the silver as chloride, in which form it was weighed. (2) The effect of precipitating the silver as chloride direct in the sulphuric acid solution with common salt, after partly neutralizing with

ammonia, was tried with practicall y the same results as obtained by the first and longer method of procedure. In either case the precipitated silver chloride was washed till the washings gave no test with silver nitrate, while the filtrates were all tested with hydrogen sulphide to be sure that the summations obtained were not due to any balancing of errors. The sulphuric acid used in the parting was tested and found to contain no nitric acid. In some cases, however, unweighable traces of platinum could be found in the filtrate, by means of an examination with a microscope on the concentrated filtrate when tested with ammonium chloride. This was neglected in our work, and no attempt was made to separate it from the silver, which it contaminated, as the amount present was very small.[1] The results follow:

Pt supposed.....	10.00	20.00	30.00	40.00	50.00
Pt actual.....	10.39	20.59	31.46	37.89[2]	57.05
Ag retained by Pt	tr.	0.59	0.98	2.24	2.70
Ag in filtrate.....	89.54	78.62	67.51	59.81	40.26
Summation	99.93	99.80	99.95	99.94	100.01

As may be seen from the previous tables, these results have been used to correct the supposed platinum percentages on the alloys.

Microstructure.—The specimens which had been reserved for the microscopic examination were next prepared for examination and photographing by polishing them successively on rough and smooth Armour emery paper, and on 0, 00, 000 and 0000 Hubert French emery paper. The polishing was finally finished on baize on a rouge board, using carefully washed jewelers' rouge. Etching was done with 1.1 specific gravity nitric acid. For examining and photographing the alloys, a Reichert microscope was used in connection with a Bausch and Lomb photomicrographic

[1] Recently in a paper published by Delépine (Compt. rend. 142, 631 (1906); abs. J. Chem. Ind. 25, 314 (1906)), it has been claimed that boiling concentrated sulphuric acid will dissolve considerable amounts of platinum on treatment for forty to fifty hours. This is in direct contradiction to other work on the same lines (Conroy: J. Chem. Ind. 22, 465 (1903)) but whether true or not has no application to our experiments where the time of treatment was much less.

[2] The very low platinum content of this alloy can only be explained by the accidental loss of platinum during the preparation, as duplicates show that the figure for platinum as given above is correct, and repeated microscopic examinations of polished sections show that it is homogeneous.

camera, using a Welsbach illumination and an inside illuminator. All photographs were taken at a magnification of 100 diameters.

Results of Thermal Analysis and Microscopic Examination.—Heycock and Neville,[1] in their investigation of a limited portion of the platinum silver cooling curve, found that with increasing platinum content, up to the limit of their investigation, the melting-point rose regularly, their alloy of maximum platinum content (3.55 per cent.) having a melting-point of 990°. In our experiments the alloy containing 10.39 per cent. of platinum was heated to 1200°, and the cooling curve taken from that point. Two evolutions of heat were noticed, the first at 1045–1050° and the second and much larger at 1000°. Owing to the conditions of radiation from the furnace there was always a slight drop of temperature throughout, when operating with weights of alloys as small as 10 grams, and it was not possible to determine whether solidification was complete at 1000° or not. The alloy, when examined under the microscope, was found to consist of crystals set in a ground mass, which was not composite, or at least, which could not be resolved by the highest power available. This is not, however, a positive proof that the ground mass had not frozen out as a eutectic and afterward become simple by segregation, a fact of common occurrence when the eutectic is small in amount. The 20.59 per cent. alloy was heated to 1100°, and on cooling evolved heat strongly at 1085°, and possibly again at 995°, although the indications at the latter point were hardly beyond the experimental error. The microstructure at this point showed large, white dendrites also set in a non-composite ground mass. The 31.46 per cent. alloy was heated to 1300° and a cooling curve taken down to 970°. Marked evolutions of heat took place in the range between 1170° and 1100°. They were, however, very irregular and were different in their exact location in different trials. The examination of the alloys under the microscope showed well-defined crystals of a grayish color set in a dark ground mass. These gray crystals had each a perfectly white silvery core or spine, which offers a clue to the irregularities of the cooling curves. This is, that the rate of cooling was so rapid that the alloy passing through transformation points did not have time to come to equilibrium, and this result is shown both by the microstructure and by the cooling curves. In the cooling curves this is shown

[1] Loc. cit.

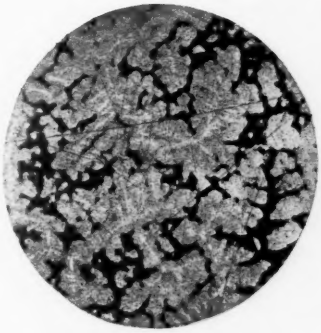
by the heat liberations at any one temperature being very small and also confused, owing to heat liberations from two separate causes taking place at the same time in different parts of the button. The most regular of the curves show, however, a consistent evolution of heat at 1160°, and this is taken as probably correct. There are also weak indications at about 1230°. In the microphotographs this is shown by the white core in the centre of the crystals, which disappears when the alloy is remelted and allowed to solidify and cool very slowly in a gas furnace (see photomicrographs). The 37.89 per cent. platinum alloy, while showing much the same characteristics in its microstructure as the 31.46 per cent. alloy, *i. e.*, gray crystals with white centres set in a dark ground mass, gives much sharper heat evolutions during its cooling. These are at 1240°, not very strong but consistent for all curves, and a second at 1170°, which is strongly marked in all curves, and is the most marked evolution for this particular alloy. Unfortunately, the curve was only once continued below 1000°, and in this case was too irregular to be of any value. The 57.05 per cent. alloy was heated to over 1400°, and on cooling gave evolutions of heat at 1240°, 1180° and 1090°. In microstructure it appeared very much like the 37 per cent. alloy.

SOLUBILITY TESTS IN NITRIC ACID.

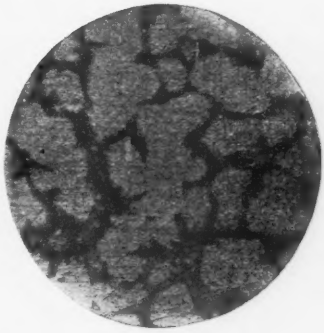
Method of Procedure.—Chemically pure nitric acid was diluted with distilled water and, after cooling, the concentration was adjusted with water to 1.1 specific gravity to within the limit of accuracy of a delicate hydrometer. Three hundred mg. of each of the alloys, cut into small pieces (1×2×2 mm.) were next weighed out into No. 2 beakers and 25 cc. of the 1.1 acid added to each. These were placed on an electric hot plate and heated rapidly to 70° or 80° and kept at that temperature for an hour, the temperature being observed by means of thermometers. At the end of twenty minutes the alloys were broken up by means of the thermometers, so as to prevent as far as possible the effect of any mechanical coating. After an hour the solutions were removed from the stove and allowed to stand for one and one-quarter hours after diluting to about 75 cc. The solutions were all somewhat colored, those from the 20 and 31 per cent. alloys especially, the order of decreasing intensity of color being 20, 31, 37, 57 and 10. Of these the 20 was almost black and was

10.39 per cent platinum.
Air cooled.

20 59 per cent. platinum.
Air-cooled.

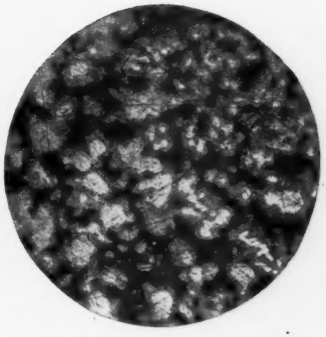


31.46 per cent. platinum.
Air-cooled.



31.46 per cent. platinum.
Furnace-cooled.

37 89 per cent. platinum.
Air cooled.



57.05 per cent. platinum.
Air-cooled.

opaque, the remainder rapidly shaded down in color to the 10, which was almost colorless. The solutions were then filtered through 7 cm. ashless filter-papers, when it was found that the filtrates bore the same color relation as the original solutions. On attempting to wash the precipitates with distilled water, they washed through the paper readily and acted in the manner common to all colloidal precipitates. The filtrates and wash solutions were therefore combined and the residues salted out with sodium nitrate free from chloride. After standing they were filtered through the same filter-paper as before, and on washing with 1 per cent. nitric acid (*i. e.*, 1 cc. of 1.42 acid in 100 of water) it was found that they could be washed free from silver without loss from the formation of any colloidal precipitate. After ignition in porcelain crucibles they were weighed, dissolved in aqua regia and the silver contained determined as in the case of the analysis of the alloys. During the ignition, slight explosions due to the precipitate reacting with the filter-paper could always be noticed. The results follow, the one given for the 31.46 per cent. alloy being determined on the alloy in the rapidly cooled state.

Per cent. Pt in alloy.....	10.39	20.59	31.46	37.89	57.05
" " residue.....	3.86	8.58	36.59	49.13	65.16
" " Ag in residue.....	0.27	1.81	12.09	13.64	12.19
" " Pt in residue.....	3.59	6.77	24.50	35.49	52.97

Evidently, from the foregoing any ratio of platinum and silver which will allow of complete solution of both in nitric acid of 1.1 specific gravity must lie within considerably closer ranges than those investigated above. A further series of alloys was therefore made in order to test further for this point. These alloys were made in the same way as the previous set and were examined microscopically for homogeneity. Parting tests were conducted as before with nitric acid of 1.1 specific gravity, except that the silver content of the residues was not determined, as the object was to find a completely soluble ratio, or failing that the most nearly soluble ratio to test the process as a means for analytical separation. Since Miller's[1] work had shown that with a platinum content of 4 per cent. some residue was left, the alloys below that point were investigated thoroughly. Besides these, alloys were

[1] Loc. cit.

made at ratios selected by means of the cooling curves and certain alloys were selected arbitrarily in order that the solubility results might not have to be interpolated except over very narrow ranges. The results follow, those for the 31.46 per cent. alloy in this case being on the very slowly cooled alloy.

Per cent.	Pt in alloy....	0.50	1.00	2.00	3.00	4.00	5.00	
" "	residue.....	0.42	0.85	1.74	2.19	2.98	3.56	
" "	Pt in alloy....	13.00	14.00	15.00	16.00	18.00	25.00	31.46
" "	residue.....	3.33[1]	4.26	4.32	4.55[1]	4.54[1]	16.62	38.58

In these tests as well as those of the previous series the formation of colloidal platinum was very marked, especially with the alloys near to 20 per cent. of platinum. When this had been completely removed by means of ammonium nitrate and heat, the solutions were still colored, but this coloration was very slight and no further separation took place in solutions containing considerable ammonium nitrate and nitric acid, even on standing several days.

As previous investigators had found that the amount of residue varied with the strength of acid used, a further series was run, using nitric acid of 1.40 specific gravity as a solvent. The method of procedure was the same as that of the previous series, the results being as follows:

Per cent.	Pt in alloy	0.50	1.00	2.00	3.00	4.00	5.00	10.00
" "	residue.....	0.22	0.42	1.09	1.81	2.42	2.62	4.53
" "	Pt in alloy	13.00	14.00	15.00	16.00	18.00	20.00	25.00	30.00
" "	residue.....	5.79	4.97	7.93	11.54	11.65	13.94	20.66	29.29

The foregoing results show clearly the impossibility of separating platinum from gold, iridium, etc., when alloyed with silver by means of one parting with nitric acid, and also the fallacy of assay methods, such as Perry's, based on this supposed separation. The questions as to the explanation of the solubilities are, however, more complex. From the results of etching tests made on the stage of the microscope it is apparent that the reaction of the alloy with the nitric acid is a double one, part tending to give solution of the alloy and part tending to produce the explosive nitro compound, well-known as one of the products of this reaction. This in itself would explain many of the differences shown by the work of various investigators working on alloys of

[1] Average of two figures.

the same composition. A second cause enters in, however, which is probably the more important. It is as follows: From the thermal data and microstructure it may be seen that the alloys consist of a series of solid solutions, having several reaction or transformation temperatures where the crystals already separated out react with the molten part of the alloy. On account of the high melting-point of these alloys, the cooling through these ranges is always so rapid that these reactions are never complete and the final alloy consists of a variety of products upon whose individual solubilities depend the solubility of the alloy as a whole.

Attempts were made to isolate the different components of the alloys by means of solution with various reagents. These were, however, all futile, as it was not possible to find in the time at our disposal, any reagent which would give a complete solution of one constituent without attack on the remainder of the alloy. In the course of this work the 37.89 and 57.05 per cent. platinum alloys were remelted and quenched in cold water from the molten state, and polished slips were submitted to the action of nitric acid of 1.2 specific gravity in the cold for a period of about ten days, the object being to isolate the constituent first to freeze out. The acid was changed frequently and the products of the reaction were removed by washing by decantation with cold water. The slips of alloy, even after being so disintegrated that they felt apart on being pressed with a stirring rod, retained their brighl appearance, showing that one constituent at least was apparently unattacked by the acid. In no case was it possible, however, to carry the treatment so far that standing in fresh acid for twenty-four hours gave no attack, as shown by the presence of silver in the solution. Whether this was due to some attack on the apparently insoluble constituent or to the continued solution of undissolved ground mass could not be determined. The residues were finally washed thoroughly and examined under a microscope when they were found to consist of grains which were apparently unattacked. Analysis of these grains while, sufficiently concordant to point to a definite platinum silver compound, did not justify the assignment of a formula. Coupled with the marked and increasing hardness and brittleness of the alloys containing more than 30 per cent. of platinum, which properties are lacking in both of the metals forming the alloys and persist

even in the annealed samples, we are led to conclude that a platinum silver compound crystallizes out which reacts against the liquid during solidification, giving a soluble or partially soluble product, which in turn further reacts or is transformed. The explanation of the abnormal solubilities of these alloys and of the widely differing results of the different investigators therefore lies in the presence of varying amounts of these constituents, depending both upon the composition and rate of cooling of the alloy.

CONCLUSIONS.

(1) The separation of platinum from gold, iridium, etc., in one operation by means of alloying with silver and parting with nitric acid is impossible.

(2) Analytical results on platinum silver alloys, based on parting with concentrated sulphuric acid, are incorrect for alloys containing 20 per cent. or more of platinum, unless correction is made for the undissolved silver remaining with the platinum.

(3) The existence of platinum silver compounds is probably the explanation of the irregular results obtained in parting with nitric acid.

QUANTITATIVE LABORATORY, COLUMBIA UNIVERSITY,
June 27, 1906.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 128.]

THE INSOLUBLE CHROMICYANIDES.[1]

BY FREDERICK VAN DYKE CRUSER AND EDMUND H. MILLER.

Received June 7, 1906.

As the potassium salt of hydrochromicyanic acid was used to precipitate the others, the methods of preparing the salts were first considered.

In 1903 L. O. Beatty investigated the method of preparation of potassium chromicyanide, and found that the methods of Böckmann,[2] Stridsberg,[3] Kaiser[4] and Christensen[5] did not give

[1] Read at the May Meeting of the New York Section of the American Chemical Society.

[2] Traité de Chimique Organique, J. Liebig, Vol. I, p. 174; Gmelin's "Handbook of Chemistry," Vol. VII, p. 420; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 1864, Vol. XVII, p. 302.

[3] Jahresb. 1864, Vol. XVII, p. 304; N. Arch. ph. nat. XXII, p. 151.

[4] Ann. Chem. Pharm. III suppl., p. 163; Gmelin Handb. 4

satisfactory results. The method finally adopted by him was a modification of the method of Christensen, which is as follows:

The chromium chloride and potassium chloride obtained by reduction of 50 grams of potassium dichromate with alcohol and hydrochloric acid, after evaporation, were dissolved in 150 cc. of water. This solution was heated, and added slowly to a hot solution of 100 grams of potassium cyanide dissolved in 200 cc. of water, stirring constantly. The mixture was digested hot for several hours. This was filtered, and evaporated *in vacuo* to concentration, filtered from the separated chromium hydroxide, and cooled in an ice mixture. The crystals were filtered off, and washed first with dilute (50 per cent.), and then with strong alcohol (95 per cent.). No alcohol was used for precipitating the salt. The salt was recrystallized as often as necessary to free it from potassium chloride. Contrary to what Kaiser states, Beatty says that the potassium chromicyanide is decomposed by boiling even in a vacuum.

His yield was less than 50 per cent.

EXPERIMENTAL.

In carrying out this work, we are indebted to Mr. L. O. Beatty, who furnished some of the potassium chromicyanide. This salt was purified by recrystallizations over sulphuric acid in a vacuum.

Some potassium chromicyanide was prepared by Beatty's method, but the method finally used, after also testing Christensen's method, was a modification of the former. Sixty grams of chromium trioxide were dissolved in 150 cc. of concentrated hydrochloric acid, and 75 cc. of water. Seventy-five cc. of 95 per cent. alcohol were added to the mixture, a little at a time, and then the solution was evaporated to dryness. The residue was dissolved in 225 cc. of boiling water, and added slowly to a hot solution of 150 grams of potassium cyanide dissolved in 300 cc. of water. The solution was stirred vigorously after each addition of the chromium solution. The mixture was digested for several hours, and then filtered on a Büchner funnel. The filtrate was allowed to evaporate in the air, large yellow crystals

aufl. 4, 335; Gmelin's "Handbook of Chemistry," VII, p. 429; "Handwörterbuch d. Chem. Fehling," p. 663; Jähresb. 1864, Vol. XVII, p. 302; Chem. Centrbl., 1865, p. 259.

[5] J. pr. Chem. 139, 2, 31, 163 (1885); [2] 23, 52.

of potassium chromicyanide forming, which were very pure, and consequently required only one or two recrystallizations.

If a large excess of potassium cyanide is used, a thick, deep red solution is obtained, from which alcohol will not precipitate potassium chromicyanide, but a syrup is formed at the bottom of the dish.

The salt heated five hours at 100° in a water-jacketed air-bath did not lose in weight. When heated at 102° in an air-bath for three hours, there was no loss in weight.

Three grams heated to 147° lost 0.7 mg. At this temperature the salt has a deep reddish yellow color.

At 159° the salt began to decompose, losing 2.3 mg. in weight, the crystals turning dark in spots. The temperature was increased, and at 196° the total loss in weight was only 3.2 mg. On ignition at a red heat the substance becomes black, and melts, the residue finally having a green color (Cr_2O_3). The crystals decrepitate when strongly heated.

One gram of pure potassium chromicyanide was dissolved in 300 cc. of water, and the solution allowed to stand in the light for several weeks at the ordinary temperature. The salt slowly decomposed, the solution becoming cloudy.

One gram of the salt heated red hot in a porcelain boat in a glass tube gave no water of crystallization.

0.7026 gram of the salt was analyzed by the following method: It was decomposed by boiling with aqua regia, the solution being boiled down with concentrated hydrochloric acid several times to get rid of the excess of nitric acid. The solution was finally diluted with water, and the chromium precipitated three times from the boiling hot solution by ammonium hydroxide in slightest excess. The filtrates were evaporated to dryness, and ignited to drive off the ammonium salts, the residue taken up with water, evaporated again, and ignited. The weight of the impure potassium chloride gave 36.3 per cent. of potassium.

The residue was dissolved in hot water, an excess of chlorplatinic acid added, and the solution evaporated. More chlorplatinic acid was added, then alcohol, until about 75 per cent. by volume, and the solution allowed to stand over night in a platinum dish. The potassium chlorplatinate was filtered, washed, dissolved by boiling water into a weighed platinum dish,

and after evaporation, weighed. Weighing the potassium as sulphate did not give satisfactory results.

The precipitate of chromium hydroxide was washed into a porcelain casserole, and treated with an excess of sodium peroxide. The solution was boiled for fifteen to twenty minutes, after the addition of more peroxide.

The solution was allowed to cool, and then diluted with water to 500 cc. volume. This was made acid by 10 cc. of concentrated sulphuric acid in excess, and titrated by a standard solution of ferrous sulphate (64.052 grams per liter), using a spot test, with a very dilute, freshly prepared solution of potassium ferricyanide. The ferrous sulphate was standardized at the same time by titration against a weighed quantity of potassium chromate, using the above conditions. This was the method used for the determination of chromium throughout the work.

Before this method was decided upon, 0.5207 gram of potassium chromate was dissolved in water, the chromium reduced in a hydrochloric acid solution by alcohol, and precipitated as chromium hydroxide. This was treated as above (sodium peroxide, etc.), and required the same number of cubic centimeters of ferrous sulphate solution as the same weight of potassium chromate, both solutions being titrated under the same conditions.

The addition of an excess of Mohr's salt to the acid chromate solution, and subsequent titration with a standard potassium permanganate solution, did not give accurate results, as the end point was obscured by the green chromium salt formed. When the precipitated chromium hydroxide was ignited and the chromium weighed as sesquioxide, the results were slightly high, due to the occlusion of salts by the hydroxide, sulphates especially causing this trouble.

The nitrogen was determined by the Kjeldahl method, using 0.5005 gram for analysis.

		Calculated. Per cent.		Found. Per cent.
3K	117.45	36.05		36.01
Cr	52.1	15.99		16.03
6C	72.0	22.1	by difference	21.97
6N	84.24	25.86		25.99
		100.00		100.00

The formula $K_3Cr(CN)_6$ is therefore confirmed.

The following reagents were used for determining the chemical properties of the chromicyanides.

Concentrated hydrochloric acid, sp. gr. 1.20; concentrated nitric acid, sp. gr. 1.42; concentrated sulphuric acid, sp. gr. 1.84; dilute hydrochloric acid, sp. gr. 1.0815; dilute nitric acid, sp. gr. 1.232; dilute sulphuric acid, sp. gr. 1.186; acetic acid, sp. gr. 1.017; ammonium hydroxide (strong), sp. gr. 0.900; ammonium hydroxide (dilute), sp. gr. 0.9775.

Double normal sodium hydroxide; double normal sodium carbonate; normal potassium cyanide; aqua regia (1 part concentrated nitric + 3 parts concentrated hydrochloric acid); sodium peroxide; ammonium sulphide.

Potassium chromicyanide is decomposed by boiling with water and sodium peroxide. The solution, made acid with acetic acid, gives a yellow precipitate with lead acetate.

It is decomposed by concentrated hydrochloric acid, in the cold, more readily on boiling, giving a green solution.

It is decomposed by concentrated nitric acid, giving a green solution on boiling.

It dissolves slowly in concentrated sulphuric acid, giving a yellow solution, which, on boiling, decomposes, giving a red, violet, and then a green solution.

It is decomposed by dilute sulphuric, hydrochloric or nitric acids, giving a green solution readily on boiling.

Aqua regia decomposes the salt more readily on heating.

Cadmium Chromicyanide, $Cd_3Cr_2(CN)_{12}$.—According to Kaiser[1] cadmium salts give a white precipitate. We prepared the salt, first, by adding a 4 per cent. solution of cadmium chloride to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of cadmium chloride. In both cases, a white precipitate with a slightly greenish tinge immediately formed. This was washed thoroughly by decantation and dried at 100°.

The compound decomposed readily on ignition in a porcelain crucible, giving cadmium oxide and metallic cadmium which deposited on the cover of the crucible. Consequently, this method could not be used for decomposing the compound for analysis.

For analysis about 0.4 gram of the substance was decomposed by dissolving in dilute hydrochloric acid and evaporating twice

[1] Ann, III Suppl., p. 170.

to a small bulk to secure complete decomposition. The cadmium was then precipitated as sulphide, the latter dissolved in dilute hydrochloric acid, and after evaporation, neutralization and the addition of 1 gram of potassium cyanide, the solution was electrolyzed by 0.17 ampere and 3.75 volts. The chromium was determined as already described.

The analyses gave: Cd, 41.45, 41.72; Cr, 12.76, 12.93. Calculated for $Cd_3Cr_2(CN)_{12}$: Cd, 44.73; Cr, 13.82. Ratio of Cr to Cd: I, 2:3.01; II, 2:2.99.

The formula given to the compound, therefore, is $Cd_3Cr_2(CN)_{12}$.

Cadmium chromicyanide is readily soluble in an excess of potassium cyanide, and ammonium hydroxide.

Concentrated hydrochloric acid immediately decomposes it, giving a red solution, which becomes green. This takes place more quickly on boiling. Concentrated nitric acid has the same effect, but the action is slower in the cold. Concentrated sulphuric acid acts more slowly than either of the above.

Dilute hydrochloric, nitric and sulphuric acids decompose the compound, giving off hydrocyanic acid, and forming green solutions quickly on boiling, but slowly in the cold. Aqua regia dissolves it quickly. On boiling with sodium peroxide, it is decomposed.

The compound is decomposed by ammonium sulphide, sodium hydroxide and sodium carbonate.

Acetic acid decomposes the compound slowly on boiling.

Cobalt Chromicyanide, $Co_3Cr_2(CN)_{12}$.—Berzelius[1] states that cobalt salts give a brown precipitate, which remains brown when dry. As given in Watts' Dictionary,[2] chromicyanide of cobalt is a blue precipitate. According to Gmelin,[3] salts of protoxide of cobalt yield a blue precipitate with sesquicyanide of chromium. Kaiser[4] states that cobalt salts give with potassium chromicyanide a flesh-colored precipitate insoluble in acids, but soluble in ammonium hydroxide, giving a yellow solution. The salt was prepared, first, by adding a 4 per cent. solution of cobalt nitrate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a

[1] Berzelius Lehrbuch, 1845, Vol. III, p. 1075.

[2] Watt's Dict. Chem., Vol. II, 1872, p. 205.

[3] Gmelin's "Handbook of Chemistry," Vol. VII, p. 495.

[4] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663: Jahresb., 1864, p. 302.

4 per cent. solution of cobalt nitrate. In both cases a light rose-colored precipitate was formed. These were washed thoroughly by decantation, magnesium chloride being added from time to time when the precipitate became colloidal, and dried at 100°. The color of the dried sample was yellowish brown.

For analysis, 0.3 to 0.5 gram was ignited in a porcelain crucible, and fused with sodium peroxide. The fusion was leached out with water, and the precipitate filtered, washed and dissolved in dilute sulphuric acid. After neutralization, 100 cc. of ammonium hydroxide and 3 grams of ammonium sulphate were added, and the solution electrolyzed by 2.5 amperes and 4.75 volts. The chromium was determined as before.

The analyses gave: Co, 22.86, 21.64; Cr, 13.59, 12.65. Calculated for $Co_3Cr_2(CN)_{12}$: Co, 29.81; Cr, 17.55. Ratio of Cr to Co: I, 2:97; II, 2:3.02.

The formula $Co_3Cr_2(CN)_{12}$ is therefore given to the compound when precipitated either by an excess of the cobalt salt or the potassium chromicyanide.

Cobalt chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by boiling with sodium peroxide, giving a black precipitate, and a yellow solution of chromate. It is also decomposed by ammonium sulphide. Ammonium hydroxide decomposes the compound, but does not entirely dissolve it. Sodium hydroxide decomposes the compound rapidly, sodium carbonate slowly. It is insoluble in cold or boiling acetic acid. Concentrated sulphuric acid, and concentrated hydrochloric acid dissolve it in the cold, very readily on boiling. It is not readily soluble in concentrated nitric acid, even on boiling.

Aqua regia decomposes the compound, but it is not entirely dissolved, even on boiling. It is very slowly soluble in dilute sulphuric, hydrochloric, or nitric acids, being least soluble in the last. On boiling, dilute sulphuric and hydrochloric acids readily dissolve it, but nitric acid, only slowly.

Cuprous Chromicyanide, $Cu_3Cr(CN)_6$.—Kaiser[1] states that by treating cupric chromicyanide with a stream of hydrogen sulphide, or by sulphurous acid, a red compound is formed, which is probably cuprous chromicyanide ($3Cu_2Cy.Cr_2Cy_3$, equivalent to $Cu_3Cr(CN)_6$ at present).

One gram of potassium chromicyanide was treated with a

[1] Ann. III Suppl., p. 166.

slight excess of a solution of cuprous chloride, in about 75 cc. bulk. An orange-yellow precipitate immediately formed, which was filtered, washed thoroughly, and dried at 100°. For analysis, about 0.5 gram was dissolved in dilute nitric acid, evaporated to low bulk, water added, and a little ammonium hydroxide, and the solution electrolyzed, using a current of 0.35 ampere and 2.1 volts.

Some chromium was oxidized by the current to chromate. Consequently, after all the copper was deposited, the electrolyte was boiled with alcohol, and then the chromium precipitated as chromium hydroxide, and determined as before.

The analysis gave: Cu, 45.01; Cr, 12.24. Calculated for $Cu_3Cr(CN)_6$: Cu, 47.80; Cr, 13.05. Ratio of Cr to Cu, 1:3.01. The formula of the compound is therefore $Cu_3Cr(CN)_6$.

Cuprous chromicyanide is readily soluble in an excess of potassium cyanide and readily dissolved by concentrated nitric acid in the cold or on boiling. Dilute nitric acid dissolves it, very quickly on boiling. It is readily decomposed by aqua regia, giving a green solution. It is decomposed by concentrated hydrochloric acid, slowly going into solution in the cold, but quickly on boiling. The dilute acid acts similarly.

Cold concentrated sulphuric acid dissolves it slowly, but quickly on boiling. The dilute acid acts similarly, but more slowly than with the concentrated acid. On boiling with the dilute acid it dissolves quickly, giving a green solution.

Cupric Chromicyanide, $Cu_3Cr_2(CN)_{12}$.—Kaiser[1] states that in the cold, copper sulphate gives a blue precipitate, containing a little potassium, as shown by his analysis, and which he calculates to copper. By mixing at 75° a concentrated solution of a copper salt with dilute potassium chromicyanide solution, the precipitate was free from potassium.

From his analysis he gives the formula $3CuCy.Cr_2Cy_3$, corresponding to $Cu_3Cr_2(CN)_{12}$ at the present time.

On heating this compound formed in the cold, at 40°, it loses water irregularly, and if the temperature is raised, it changes from blue to blue-green, green, yellow-green, and finally reddish-gray at 100°, carrying variable amounts of water. This red salt, on being treated with water, will not become blue again. It is

[1] Ann. III Suppl., p. 166; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

insoluble in cold acids, dilute or concentrated, but dissolves on heating. Also insoluble in cold ammonium hydroxide, and sodium hydroxide. On boiling with the latter, dark brown copper oxide is finally precipitated.

Comey[1] gives the formula $Cu_3(Cr(CN)_6)_2$ to the cupric compound, and states that it is a precipitate insoluble in dilute or concentrated acids, except on heating; insoluble in ammonium or potassium hydroxides plus water.

We prepared the salt, first, by adding a 3 per cent. solution of copper sulphate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 3 per cent. solution of potassium chromicyanide to a 2 per cent. solution of copper sulphate. In both cases, a precipitate immediately formed, having a robin's egg-blue color, which changed to green on standing. Both precipitates were thoroughly washed by decantation, potassium sulphate and magnesium chloride being used with the latter as it became very colloidal, and dried at 100°. The color of the dried substance was reddish purple.

For analysis, about 0.5 gram was dissolved in dilute nitric acid, and after boiling for about two hours, the solution was electrolyzed. The chromium was precipitated as hydroxide, and determined as usual.

The analyses gave: Cu, 32.23, 30.96; Cr, 17.50, 16.96. Calculated for $Cu_3Cr_2(CN)_{12}$: Cu, 31.41; Cr, 17.15. Ratio of Cr to Cu: I, 2:3.02; II, 2:2.99.

The formula $Cu_3Cr_2(CN)_{12}$ is therefore given to this compound, being precipitated either by an excess of the copper salt, or *vice versa*.

Cupric chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by an excess of ammonium hydroxide in the cold, giving a blue solution, and a precipitate. Ammonium sulphide gives a black precipitate of copper sulphide. It is decomposed by sodium hydroxide, and by sodium carbonate, the latter giving a blue solution, and a yellowish green precipitate.

It is dissolved by aqua regia; readily by concentrated sulphuric acid in the cold, giving a red solution, which becomes violet, and finally green. Concentrated hydrochloric acid readily dissolves it in the cold, more quickly on boiling. Concentrated nitric acid decomposes it, but only gives a clear green solution on boiling. It

[1] "Dictionary of Solubilities," 1896.

is very slowly soluble in cold dilute hydrochloric, nitric, and sulphuric acids, while on boiling the first two readily dissolve it, but the sulphuric acid dissolves it only slowly. It is insoluble in cold acetic acid.

Boiled with sodium peroxide and water, it is decomposed, giving a green solution. On the addition of acetic acid, a precipitate formed. This was removed by filtration and then lead acetate added to the filtrate, and a yellow precipitate of lead chromate obtained.

Ferrous Chromicyanide, $Fe_3Cr_2(CN)_{12}$.—According to Kaiser,[1] potassium chromicyanide gives with ferrous solutions, a red, very pulverulent precipitate. If precipitated at 70° it is practically potassium-free, two analyses averaging 0.25 per cent. of potassium. If heated to 100° there is a great loss of hydrocyanic acid, and the black mass resulting no longer dissolves by warming with hydrochloric acid, while the compound dried over sulphuric acid readily dissolves in hydrochloric acid. To the substance dried over sulphuric acid he gives the formula $3FeCN.Cr_2(CN)_3.20Aq.$, corresponding to $Fe_3Cr_2(CN)_{12}.20Aq.$ at the present time, but states that the point at which the compound has not yet lost any water is very difficult to determine accurately, because the substance contains so much water of crystallization. The substance is decomposed by shaking with sodium hydroxide. Liebig[2] states that potassium chromicyanide gives a brick-red precipitate with ferrous salts. Watts[3] states that the precipitate is brick-red, while Storer[4] gives the formula $3FeCN.Cr_2(CN)_3$ (?), equivalent to $Fe_3Cr_2(CN)_{12}$ at present.

We prepared the salt, first, by adding a 7 per cent. solution of Mohr's salt to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 4 per cent. solution of Mohr's salt. In both cases, two drops of concentrated sulphuric acid were added. A brick-red granular precipitate formed immediately in each case, which was washed thoroughly by decantation, and dried at 100°. The color of the dried substance was dark green.

[1] Ann. III Suppl., p. 169; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

[2] "Traité de Chimique Organique," J. Liebig, Vol. I, p. 174.

[3] Watt's "Dictionary of Chemistry," 2, 205 (1872).

[4] Storer: "Dictionary of Solubilities," 1864.

For analysis, from 0.3 to 0.5 gram was ignited in a porcelain crucible, fused with sodium peroxide, and the fusion leached out with water. The precipitate was filtered, washed, dissolved in sulphuric acid, and the iron determined by titration with permanganate. The chromium was determined as before.

The analyses gave: Fe, 22.12, 22.06; Cr, 13.85, 13.75. Calculated for $Fe_3Cr_2(CN)_{12}$: Fe, 28.70; Cr, 17.83. Ratio of Cr to Fe: I, 2:2.98; II, 2:2.99. Therefore, the formula of the compound is $Fe_3Cr_2(CN)_{12}$.

Ferrous chromicyanide is decomposed by sodium hydroxide and ammonium hydroxide, giving a brown precipitate, by sodium carbonate giving a green precipitate, and by ammonium sulphide. Potassium cyanide immediately turns the precipitate dark-red, but does not dissolve it. It is decomposed by boiling with sodium peroxide and water.

Aqua regia immediately decomposes the compound, in the cold or on boiling. It is most soluble in hydrochloric acid, concentrated or dilute acid slowly dissolving it in the cold, but very quickly on boiling, giving a green solution.

Dilute or concentrated nitric acid, in the cold, decomposes it, giving a precipitate of a dirty yellow color. On boiling with the dilute acid, a clear solution is obtained, but the precipitate does not dissolve on boiling with the concentrated acid, except when diluted with water. Concentrated sulphuric acid immediately decomposes it, hot or cold. Cold dilute sulphuric acid acts more slowly than hydrochloric acid but, on boiling, a clear solution is quickly obtained. It is not decomposed by cold acetic acid.

Manganous Chromicyanide, $Mn_3Cr_2(CN)_{12}$.—Kaiser[1] states that the manganese salt is white, crystalline, and insoluble in dilute acids.

We prepared the salt, first, by adding a $3\frac{1}{2}$ per cent. solution of manganese chloride to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of manganese chloride. In both cases, a greenish white precipitate immediately formed, which, under the microscope, appeared to consist of small crystals, apparently isometric. The precipitates were washed thoroughly, and dried at 100°; when dried, the color was light brown.

[1] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

If the compound is dried in a desiccator, in a vacuum, over sulphuric acid, it has a buff color.

The compound was analyzed by several methods. A portion was ignited in a porcelain crucible, and then fused with sodium peroxide, but this introduced silica and alumina, which had to be subsequently separated, and the results were very poor. Another portion was dissolved in hydrochloric acid, and the chromium precipitated four times by ammonium hydroxide. The manganese could not be separated from the chromium by this method. The filtrates were combined, the manganese separated, and potassium determined, giving only a trace.

Finally, about 0.5 gram of the compound was dissolved in dilute hydrochloric acid, and after two evaporations to low bulk with acid, sodium peroxide was added, and the solution boiled. The precipitate was filtered, washed, and dissolved in dilute hydrochloric acid and sulphurous acid. The sulphur dioxide was boiled out of the solution, and the preceding process repeated four times until the manganese was free from chromium, when it was determined as manganese pyrophosphate. The chromium was determined as before.

The analyses gave: Mn, 23.06, 23.14; Cr, 14.58, 14.69. Calculated for $Mn_3Cr_2(CN)_{12}$: Mn, 28.37; Cr, 17.91. Ratio of Cr to Mn, I, 2 : 2.99; II, 2 : 2.98.

The compound has, therefore, the formula $Mn_3Cr_2(CN)_{12}$.

The compound is decomposed by sodium peroxide, giving a precipitate of manganese dioxide, and a yellow solution of chromate; decomposed by boiling with concentrated hydrochloric, nitric or sulphuric acid or aqua regia, giving a green solution; readily soluble in an excess of potassium cyanide; decomposed by an excess of ammonium hydroxide, sodium hydroxide, sodium carbonate and ammonium sulphide; dissolves very slowly in dilute hydrochloric, nitric or sulphuric acid, but readily on boiling, giving a green solution; only slightly soluble in cold acetic acid, more so on boiling.

Mercurous Compound.—According to Berzelius,[1] mercurous salts give a white precipitate with potassium chromicyanide, which makes the solution at the bottom brown, while the precipitate becomes dark. The color of the liquid soon disappears,

[1] Berzelius' "Lehrbuch," Vol. III, p. 1075 (1845).

and a compound of chromium cyanide with a little mercury remains behind.

Kaiser[1] states that mercurous nitrate gives a dark gray precipitate with potassium chromicyanide, insoluble in nitric acid and ammonium hydroxide.

We dissolved 0.5 gram of potassium chromicyanide in 50 cc. of water, and quickly added 100 cc. of a 2 per cent. solution of mercurous nitrate.

A yellowish white precipitate formed, which quickly darkened, turning finally to gray, and which settled rapidly. The solution did not then smell of hydrocyanic acid. One hundred cc. of water were added, and the solution stirred. The precipitate settled rapidly, leaving the supernatant liquid reddish-yellow, which rapidly became darker in color. The precipitate darkened, becoming smaller in volume, and on stirring the solution hydrocyanic acid could be readily detected. On standing for a day or so the solution became green, due to the color of the chromium salt. The gray precipitate proved to be nothing but metallic mercury in a very finely divided state. This was filtered and washed, dissolved in dilute nitric acid, part of the acid neutralized by ammonium hydroxide and the solution electrolyzed by a current of 0.18 ampere, and 2.3 volts.

Total weight of mercury found was 0.4679 gram.

The reaction takes place probably in the following steps: First, mercurous chromicyanide is precipitated, which then decomposes, giving mercurous cyanide, which then decomposes, giving mercuric cyanide, which slowly dissolves, and metallic mercury.

If the reaction takes place as above stated, 0.5 gram of the potassium salt would precipitate 0.4605 gram of mercury, while 0.4679 gram was found.

Nickel Chromicyanide, $Ni_3Cr_2(CN)_{12}$.—Kaiser[1] states that solutions of nickel salts give a bluish-green precipitate, very voluminous, becoming green on boiling, insoluble in dilute acids, but soluble in ammonium hydroxide with a grayish green color.

The salt was prepared, first, by adding a 4 per cent. solution of nickel nitrate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 4 per cent. solution of nickel nitrate. In both

[1] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

cases a voluminous light greenish blue precipitate formed immediately which was washed thoroughly by decantation, with the aid of 8 grams of magnesium chloride, added from time to time, when it became too colloidal. The precipitates were dried at 100°, when they became black in color.

Five-tenths gram of the substance was dissolved by dilute nitric acid, and the separation of the chromium from the nickel attempted by the addition of ammonium hydroxide, in the presence of ammonium chloride, and reprecipitation of the chromium. The results were inaccurate. Finally 0.3 to 0.6 gram was ignited in a porcelain crucible, fused with sodium peroxide, and the fusion leached out with water. The precipitate was filtered, washed, and dissolved in dilute sulphuric acid. After the addition of 3 grams of ammonium sulphate, and 100 cc. of ammonium hydroxide in excess, the solution was electrolyzed by a current of 2.5 amperes and 3 volts. The chromium was determined as before.

The analyses gave: Ni, 24.25, 18.13; Cr, 14.37, 10.76. Calculated for $Ni_3Cr_2(CN)_{12}$: Ni, 29.71; Cr, 17.58. Ratio of Cr to Ni, I, 2:3.00; II, 2:2.99. Number II was not dry when analyzed.

The formula $Ni_3Cr_2(CN)_{12}$ is, therefore, given to the compound, being precipitated either by an excess of nickel salt or of potassium chromicyanide.

The substance is readily soluble in an excess of potassium cyanide and ammonium hydroxide. It is readily decomposed by ammonium sulphide. It dissolves slowly in the cold in dilute hydrochloric, nitric or sulphuric acid, but readily on boiling, giving a clear green solution.

It is slowly soluble in concentrated hydrochloric, nitric, or sulphuric acid, being much more soluble in concentrated sulphuric acid than in either of the other two. On boiling, all three acids readily dissolve it, forming clear green solutions.

It is slowly decomposed by aqua regia in the cold, quite readily on boiling, giving a green solution after a few minutes.

On boiling with sodium peroxide and water, it is decomposed, but not very readily, precipitating green nickel hydroxide. The filtrate contains sodium chromicyanide. Sodium hydroxide behaves similarly. Sodium carbonate decomposes it slowly in the

cold. The compound is insoluble in cold acetic acid, but is slightly soluble on boiling.

Silver Chromicyanide, $Ag_3Cr(CN)_{12}$.—Berzelius[1] states that silver salts give a white precipitate with potassium chromicyanide, which is gray when dry.

Kaiser[2] states that silver chromicyanide is of a deep yellow color, and in the dry state unaffected by light. It is noted for its stability, being unaffected after twelve hours' treatment with hydrochloric acid, nitric acid, or ammonium hydroxide. He says that the only solvent is potassium cyanide, and that hydrochloric acid reprecipitates silver chromicyanide. Dried at 20° to 30°, it retains its yellow color, while at 100° it has a rose-red color, and loses 0.6 per cent. of its weight. He gives the formula $3AgCN.Cr_2CN_3$, equivalent to $Ag_3Cr(CN)_6$ at present, and states that there was some undecomposed substance in the silver chloride, making the percentage of silver high and the chromium low. According to Watts,[3] silver nitrate gives a white precipitate.

Stover[4] gives chromicyanide of silver $3AgCN.Cr_2(CN)_3$, equivalent to $Ag_3Cr(CN)_6$ at present, as a precipitate. Comey[5] says that silver chromicyanide $Ag_3Cr(CN)_6$ is insoluble in all solvents excepting potassium cyanide.

Böckmann[6] states that potassium chromicyanide forms a white precipitate with silver salts similar in composition to the potassium salt. When heated, it decomposes into cyanogen gas, metallic silver and chromium cyanide. Hydrogen sulphide passed through the solution containing silver chromicyanide in suspension, gives silver sulphide, and hydrochromicyanic acid.

We prepared the salt by adding a 4 per cent. solution of silver nitrate to a 2 per cent. solution of potassium chromicyanide. An orange-yellow voluminous precipitate immediately formed, which settled rapidly, and was easily washed by decantation, and dried at 100°; when dry, it was rose-red in color.

Difficulty was encountered in the analysis of this compound.

[1] Berzelius' "Lehrbuch," Vol. III, 1075-76 (1845).

[2] Ann. III Suppl., p. 167; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

[3] Watts' "Dictionary of Chemistry," 2, 205 (1872).

[4] "Dictionary of Solubilities," 1864.

[5] "Dictionary of Solubilities," 1896.

[6] Gmelin's "Handbook of Chemistry," Vol. VIII, p 31; "Traité de Chimique Organique," J. Liebig, Vol. I, p. 174.

The substance was dissolved in concentrated nitric acid and dilute sulphuric acid, and heated for some time. The silver was precipitated as silver chloride, which gave about 0.7 per cent. of silver too high, and about 0.5 per cent. of chromium too low. This corresponds quite closely to the results given by Kaiser.[1] Several analyses were made with the same result. It was thought that the difficulty was with incomplete decomposition of the silver compound. Consequently, the following method was finally used, giving good results:

About 0.5 gram of the substance was treated with concentrated nitric acid and dilute sulphuric acid, the solution boiled down to low bulk, more nitric acid added, and the treatment repeated three times, finally evaporating until nearly all the nitric acid was eliminated. If the solution is evaporated too far, a sulphate of chromium will be formed, which is then insoluble on the addition of more acid and boiling. The solution was allowed to cool, and then a little dilute hydrochloric acid was added to precipitate the silver. The silver chloride was filtered on a porcelain Gooch crucible, with a piece of filter-paper on the bottom, and dried at 110° and weighed. The silver chloride was dissolved in 3.25 grams of potassium cyanide, and the solution electrolyzed.

The chromium was determined as before.

The analyses gave: Ag, from electrolysis, 60.84; from AgCl, 60.89; Cr, 9.69. Calculated for $Ag_3Cr(CN)_6$: Ag, 60.85; Cr, 9.79. Ratio of Cr to Ag: from electrolysis, 1:3.03; from AgCl, 1:3.04.

The formula $Ag_3Cr(CN)_6$ is confirmed.

Silver chromicyanide is readily soluble in an excess of potassium cyanide, giving a yellow solution. Ammonium sulphide decomposes the compound, precipitating black silver sulphide. It is decomposed by sodium hydroxide solution, and slightly by ammonium hydroxide. It is insoluble in a solution of sodium carbonate, as in hot or cold acetic acid. By boiling with sodium peroxide and water it is decomposed.

A large excess of concentrated hydrochloric acid dissolves the compound, the solution becoming red, then pink, and finally green. On dilution with water, silver chloride is precipitated. When treated with small amounts of acid the decomposition is the same,

[1] Kaiser: Ann. III Suppl., p. 167.

only silver chloride is precipitated. With concentrated nitric acid it slowly dissolves, giving a yellow solution. On boiling it quickly dissolves, giving a green solution.

It is readily soluble in an excess of concentrated sulphuric acid, the solution becoming red, then pink and finally green.

It is decomposed by aqua regia, giving a precipitate of silver chloride. It is very slightly soluble in cold dilute hydrochloric acid, but decomposes on boiling, giving a green solution and a precipitate of silver chloride. It is slightly soluble in cold dilute nitric acid, but even on boiling is not entirely dissolved. Dilute sulphuric acid does not attack it as readily as dilute nitric acid, being only very slightly soluble in the cold, but much more soluble on boiling.

Zinc Chromicyanide, $Zn_3Cr_2(CN)_{12}$.—According to Berzelius[1] zinc salts give a white precipitate with potassium chromicyanide, bluish gray when dry.

Kaiser[2] states that the zinc precipitate is yellowish white in color, pulverulent, and easily soluble in ammonium and sodium hydroxides, but only incompletely decomposed by alkali carbonates. It is insoluble in dilute acids, but somewhat concentrated acids color the compound red, and the solution also.

Gmelin[3] says that the zinc compound is white, turning light bluish gray when dry.

Storer[4] says that chromicyanide of zinc is a precipitate.

Watts[5] states that a solution of potassium chromicyanide gives a white precipitate with zinc salts.

We prepared the salt, first, by adding a 4 per cent. solution of zinc sulphate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of zinc sulphate. In both cases, a yellowish white precipitate immediately formed, which, under the microscope, appeared to consist of very small crystals, apparently isometric. The precipitates were thoroughly washed and dried at 100°. When dried over sulphuric acid, at the ordinary temperature, the compound has a straw color.

[1] Berzelius' "Lehrbuch," Vol. III, p. 1075 (1845).

[2] Ann. III Suppl., p. 169; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

[3] Gmelin's "Handbook of Chemistry," Vol. VII, p. 425.

[4] Storer's "Dictionary of Solubilities," 1864.

[5] Watts' "Dictionary," Vol. II, p. 205 (1872).

About 0.5 gram of the substance was dissolved in sulphuric acid, and the chromium precipitated four times by ammonium hydroxide, dissolving the precipitate each time in a considerable excess of hydrochloric acid. From the results obtained it was found that the separation of chromium from zinc was not complete.

Another sample was analyzed as before, with the exception that the zinc was precipitated first as sulphide after taking out the chromium as before. The sulphide of zinc was dissolved in hydrochloric acid, and the zinc precipitated as before. The results again showed incomplete separation of chromium and zinc. Finally about 0.5 gram of the substance was dissolved in aqua regia, and the solution boiled down to low bulk several times in a casserole after the addition of hydrochloric acid. The solution was finally diluted with water to a volume of about 400 cc., and neutralized by ammonium hydroxide, and then made fairly acid with acetic acid, and a stream of hydrogen sulphide passed through the solution in the cold for about two hours.

The zinc sulphide was filtered, washed, and dissolved in hydrochloric acid, and the zinc determined as pyrophosphate. The chromium was determined as before. Potassium was determined as chlorplatinate, giving 0.35 per cent. of potassium, which was somewhat impure from a little organic matter from the alcohol.

The analyses gave: Zn, 29.42, 31.01; Cr, 15.68, 16.41. Calculated for $Zn_3Cr_2(CN)_{12}$: Zn, 32.01; Cr, 17.00. Ratio of Cr to Zn: I, 2 : 2.99; II, 2 : 3.01.

The formula of the compound is therefore $Zn_3Cr_2(CN)_{12}$.

Zinc chromicyanide is readily soluble in an excess of potassium cyanide, sodium hydroxide, and ammonium hydroxide. It is decomposed by sodium carbonate solution. Ammonium sulphide decomposes the compound, precipitating white zinc sulphide. Boiled with sodium peroxide and water it gives a clear yellow solution, which yields a yellow precipitate of lead chromate on the addition of lead acetate and acetic acid.

With concentrated hydrochloric acid it decomposes slowly, but very quickly on boiling, giving a red, then green solution. It is readily decomposed by boiling with concentrated nitric or sulphuric acid, giving a green solution in each case.

Aqua regia decomposes it quickly, giving a clear red solution, which becomes green.

Dilute hydrochloric acid in the cold easily dissolves the compound, yielding finally a green solution. Dilute sulphuric acid acts more slowly, while dilute nitric acid decomposes it very slowly. On boiling, any of the three readily yields a green solution. It is very slightly soluble in boiling acetic acid.

Lead Compounds.—Böckmann[1] states that potassium chromicyanide gives a white precipitate with basic lead acetate, but no precipitate with lead nitrate. Berzelius[2] says that lead salts give a white precipitate, which becomes blue on drying. Kaiser[3] states that the neutral lead salt is soluble in water. On evaporation, hydrocyanic acid is given off, the solution becomes green and a grayishwhite pulverulent substance separates. He says that it is easy to obtain a basic lead chromicyanide by adding to the yellow solution containing the neutral salt a mixture of lead acetate and ammonium hydroxide. Also that basic salts can be formed from hydrochromicyanic acid. He thinks that several of these basic salts exist, as on adding to the filtrates either lead acetate or ammonium hydroxide, he obtains repeatedly new compounds containing chromium. Also that the precipitates formed are sometimes easily soluble in an excess of lead solutions, or that the filtrates are precipitated by diluting with water. In other cases this did not happen. He analyzed one of the compounds, and from the results obtained concluded that it was a mixture of different basic salts. The compound was easily soluble in nitric acid and sodium hydroxide solution.

We found that tenth-normal solutions of lead nitrate and lead acetate, with a few drops of acetic acid, gave no precipitate with tenth-normal potassium chromicyanide solution, either when added in excess, or *vice versa*.

Soluble Chromicyanides.—Kaiser[3] states that mercuric chloride and stannous chloride solutions behave the same as lead. He states that aluminium, chromium, ferric iron or uranium, gives no precipitation with potassium chromicyanide in the cold, while, on heating, the potassium salt is decomposed. According to

[1] Liebig's "Traité de Chimique Organique," Vol. I, p. 174.

[2] Berzelius' "Lehrbuch," Vol. III, pp. 1075–76 (1845); Gmelin's "Handbook of Chemistry," Vol. VII, p. 428.

[3] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 303 (1864).

Böckmann[1] the salts of ferric iron give no precipitate; also given by Watts.[2]

We found that tenth-normal solutions of the following reagents gave no precipitate with tenth-normal potassium chromicyanide, either when added in excess, or *vice versa*.

Aluminium sulphate, barium chloride, calcium chloride, bismuth nitrate (with enough nitric acid to prevent hydrolysis), ferric chloride, lithium chloride, magnesium sulphate, mercuric nitrate (with a few drops of nitric acid added to dissolve the salt), mercuric chloride, strontium chloride, sodium chloride, ammonium chloride, caesium chloride, rubidium chloride, chromium chloride, arsenic acid, cerous sulphate, antimony chloride (with enough hydrochloric acid to keep the antimony in solution), antimony chloride, with enough tartaric acid to keep the antimony in solution, erbium nitrate, beryllium nitrate, didymium nitrate, ammonium molybdate, lanthanum nitrate, platinum chloride (chlorplatinic acid), sodium chlorplatinate, sodium tungstate, ammonium vanadate, uranium nitrate, columbium potassium fluoride (K_2NbOF_5), tantalum potassium fluoride (a saturated solution only), arsenious acid (a saturated solution only), stannous chloride (with enough hydrochloric acid to keep the salt in solution), thorium nitrate, thallium sulphate, yttrium nitrate, zirconium nitrate (with a few drops of nitric acid to clear the solution).

A 5 per cent. solution of palladium chloride and a solution of auric chloride gave no precipitate when added in excess, or *vice versa*, to a tenth-normal solution of potassium chromicyanide.

From the foregoing results, we see that the insoluble chromicyanides, formed by the ordinary methods of precipitation, are all normal in composition, in this respect as well as regards their solubility, resembling the cobalticyanides more closely than the ferricyanides. The fact of their normal composition, and the intense red color of the ferrous compound, may lead to their use in volumetric analysis, but whether they are insoluble enough to give accurate results further investigation must decide.

QUANTITATIVE LABORATORY, COLUMBIA UNIVERSITY,
June 4, 1906.

[1] Liebig's "Traité de Chimique Organique," Vol. I, p. 174.

[2] Watts' "Dictionary of Chemistry," Vol. II, p. 205 (1872).

IRON AND CALCIUM.

By Oliver P. Watts.

Received July 13, 1906.

Now that calcium has become available for experimental purposes, and could no doubt be produced cheaply enough for commercial use, provided there were a large demand for it, any new experiments with this metal, although they have yielded results of no constructive value, may yet contribute something to our all too scanty knowledge of the properties and uses of this interesting element. It is with this in mind that an account of the experiments which follow is presented. One of the most promising fields for the use of calcium would seem to be in metallurgy, particularly in the metallurgy of iron, where it might prove an efficient substitute for the deoxidizing agents—silicon, manganese, and aluminum. In addition to its action as a deoxidizing agent, calcium might be expected to be of value in removing sulphur and phosphorus from iron. A proposal to use calcium for these purposes raises the question of the extent to which any excess of calcium will alloy with the iron, and its effects upon the latter metal. These are the questions concerning which some preliminary experiments have been made.

Four attempts were made to form alloys of calcium with iron by fusing together the two metals. In order to prevent oxidation of the calcium before the iron reached its melting-point, the calcium was hammered into a cavity drilled in a cylinder of pure iron, and an iron cap either screwed or hammered tightly into the opening, so that it would have required an internal pressure of several hundred pounds per square inch to force out the cap. The cylinder was placed in a crucible of Acheson graphite lined with magnesia, tightly covered with the same materials, and heated in an electric furnace of the resistance type until the iron melted. Owing to the low density of calcium, the weight of this metal used in each case was small.

	I.	II.	III.	IV.
Weight of calcium taken.....	1.6	4.5	6.0	14.3
Per cent. of calcium taken..... ...	0.23	1.4	0.77	3.78

The results as to the alloying of the two metals were uniform—no calcium was found in the melted iron. Two changes in composition were, however, made by the calcium. In IV the content

both of silicon and of carbon was increased to 0.32 per cent. silicon and 0.218 per cent. carbon. The same iron melted under like conditions, but, without the calcium, contains 0.01 to 0.09 per cent. silicon and 0.03 to 0.04 per cent. carbon, so that the actual increase was 0.83 gram silicon and 0.65 gram carbon. The first thought would naturally be that this increase of silicon and carbon was due to impurities in the calcium used, but this would require that metal to contain 5.8 per cent. silicon and 4.5 per cent. carbon. The gas evolved by the action of this calcium on water had only the faintest odor, and burned with a non-luminous flame, indicating the absence of any considerable amount of calcium carbide. The calcium came from Germany and was not analyzed by the writer, but analysis of similar metal by B. Larsen[1] gave 0.11 per cent. CaC_2. The only tenable inference seems to be that the silicon and carbon are reduction products of the action of the calcium upon silica present as impurity in the magnesia lining, and upon carbon monoxide in the atmosphere within the crucible. In previous attempts to produce alloys of iron high in aluminum, by melting together the two metals in a similar crucible buried in a carbon resistor, the reducing action upon the carbon monoxide was so great as to form large amounts of aluminum carbide. It was therefore expected that calcium would act similarly, and it is only surprising that the extent of this action was not greater. In this connection the action of calcium upon carbon dioxide was tested by kindling a thin piece of the metal in the air, which was difficult to do with the highest heat of a Bunsen burner, and plunging it into a jar of the gas. It burned brilliantly, much more so than in air, leaving as solid products, lime, calcium carbide and carbon. A further attempt at alloying iron and calcium was made by heating 2 grams of calcium within a cylinder of pure iron for seventeen hours at 850–880°. The calcium melted, but no trace of alloying was found. C. Quasebart, of Aachen,[2] also obtained negative results in several attempts to alloy calcium with iron.

As a last resort in the endeavor to alloy iron with calcium, iron oxide was reduced by calcium filings in the presence of excess of calcium. The charge, consisting of 42 grams calcium filings, 60 grams pulverized Fe_3O_4, and 20 grams of calcium in lumps,

[1] Chem. Centr. 2, 1466 (1905).

[2] Electrochem. Met. Ind. May, 1906, p. 190.

was put into a magnesia crucible. This was enclosed in a strong steel cylinder, devised by Professor C. F. Burgess for firing thermite and similar charges under great pressure, and kindly placed at the disposal of the author. The charge was fired electrically by means of an iron fuse-wire. The reaction was very vigorous and resulted in a metallic ingot and several small pellets. In cold water gas was slowly evolved from the metal at a few points on the surface and calcium hydroxide was formed. For analysis a small piece was heated for three hours in water until all evolution of gas had ceased. It was then washed, dissolved in hydrochloric acid, and found to contain 0.3 per cent. of calcium. Although this amount of calcium came from the interior of the mass of metal, in view of the failure of all other attempts to make an alloy it seems probable that the calcium was imprisoned by the sudden cooling after reaction occurred and held mechanically, not alloyed with the iron.

The diffusion of phosphide of iron through solid iron at high temperatures has been pointed out by J. O. Arnold.[1] Experiments were tried to see if calcium, when heated in contact with iron containing phosphorus and sulphur, would diminish the amounts of these elements sufficiently for the change to be detected by the microscope. To prepare metal for this treatment, coarsely pulverized electrolytic iron was mixed with sulphur and placed in a magnesia-lined crucible, while red phosphorus was enclosed in a cylinder of pure iron and placed in another crucible; both were melted in the electric furnace.

	For sulphur.	For phosphorus.
Weight of iron in charge	372.4 grams.	438.62 grams.
Weight of non-metal in charge	7.6 "	13.5 "
Percentage of non-metal in charge	2	2.76
Percentage of non-metal found	0.3	1.96
Weight of non-metal combined with iron	1.13 grams.	8.62 grams.

Holes were drilled in the ingots; into these were put 5.0 grams and 7.3 grams of calcium respectively, and the openings were closed by caps of pure iron. The ingots were packed in powdered magnesia in a crucible, and heated five hours, at 1200–1300° in a gas furnace. They were badly oxidized, particularly at the tops. All calcium had vanished and the ingot had become perfectly homogeneous, except that the boundaries of the cavity which had contained the calcium could still be distinguished.

[1] J. Iron Steel Inst. 1894, I, p. 107.

Each ingot was of the same structure throughout, the caps of pure iron having the same appearance under the microscope as the rest of the ingot. Dark areas, probably of phosphide eutectic, were distributed quite uniformly throughout the ingots. The calcium in this experiment was probably oxidized partially, and perhaps wholly, by oxide of iron.

In the same way calcium was melted with iron containing phosphorus and sulphur. Eight grams of calcium removed all of the 0.37 gram of sulphur present in one ingot, and 11 grams of calcium removed 0.61 gram out of a total of 6.04 grams of phosphorus present in the other ingot, thus reducing the percentage of the latter element from 1.96 to 1.56.

These experiments show:

1. That iron and calcium do not form alloys.

2. That by the reduction of the oxides of carbon the latter element may be introduced into fused metals to which calcium is added.

3. That any commercial application of calcium to the removal or phosphorus from iron is impracticable.

The above observations were made incidental to an investigation of iron alloys, now in progress under a grant from the Carnegie Institution.

LABORATORY OF APPLIED ELECTROCHEMISTRY,
UNIVERSITY OF WISCONSIN.

THE CONSTITUTION OF PARIS GREEN AND ITS HOMOLOGUES.

BY S. AVERY.

Received June 28, 1906.

INTRODUCTION.

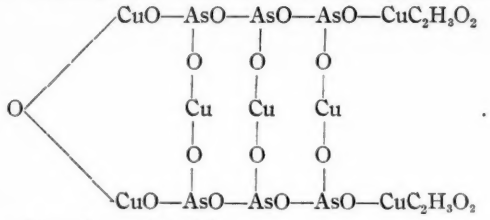
COPPER aceto-arsenite, under the names of Paris green, Schweinfurt green, and many others, has been a commercial product for nearly a century. The first contribution to its chemistry that I am able to find was made by Liebig.[1] The first definite statement in regard to its composition was made by Ehrmann,[2] working in Liebig's laboratory, who found it to consist of 3 molecules of copper meta-arsenite crystallized with 1

[1] Liebig u. Poggendorf's Handwörterbuch der reinen und angewandten Chemie, 1848, 703.

[2] Ann. 12, 92.

molecule of copper acetate. Abraham[1] found that formic, butyric or valeric acid could be substituted for acetic acid, but does not seem to have made an analysis of the products. Wöhler[2] found that in a butyric green made by him 2 molecules of copper meta-arsenite are united with one of the copper butyrate.

Speculation in regard to the constitution of Paris green have not been wanting, thus Schiff and Sestini[3] suggest the following:



Such a formula would yield

	Per cent.
As_2O_3	47.40
CuO	44.46
$C_4H_6O_3$	8.14

whereas the formula of Ehrmann requires

	Per cent.
As_2O_3	58.55
CuO	31.39
$C_4H_6O_3$	10.06

and numerous analyses of the purest samples do not show a variation of more than 3 per cent. of arsenious acid, 1 per cent. copper and 0.4 per cent. of acetic anhydride from Ehrmann's formula.

In comparatively recent years doubt has been expressed as to whether Paris green of a definite chemical composition can be produced. Six years ago the writer and Beans,[4] as the result of numerous analyses and relying to some extent on the opinions of other chemists, used the expression "Since Paris green is a compound of no very definite composition," etc. Stillman,[5] referring to Ehrmann's formula, says: "This formula is empirical, since a portion of the arsenic may exist as arsenic acid, and copper sub-

[1] Chem. News, 21, 265.
[2] Ann. 94, 44.
[3] Ann. 228, 91.
[4] This Journal, 23, 116.
[5] Chem. News, 80, 250.

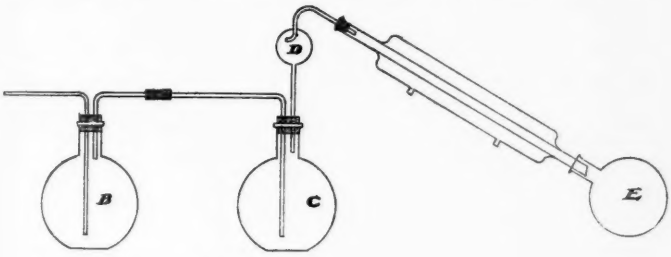
oxide may be present in small amounts with copper oxide." Later work on the part of the writer has convinced him that, while in a measure true, both of the above statements give an erroneous impression. In particular, I have never been able to detect more than minute traces of arsenic acid or cuprous oxide in any carefully prepared samples. However, the variation from Ehrmann's formula in the case of some samples is too great to be explained on the assumption of impurities present in the samples. The present paper presents an attempt to explain these variations and to throw light on the constitution of these important compounds.

EXPERIMENTAL PART.

The analytical methods employed were as follows: The sample in which arsenic was to be determined was dissolved in the smallest possible amount of very dilute sulphuric acid, heating on the water-bath, if necessary. The resulting solution was titrated with standard iodine solution according to the method of the writer and Beans.[1] The presence of a tartrate as given in this method permits of the titration of arsenites containing zinc, nickel, or cobalt in solution as well as copper.

The copper determinations were made by electrolysis of samples from which the arsenic had practically all been volatilized by evaporating nearly to dryness on the water-bath with the addition of strong hydrochloric acid. The copper chloride was then converted into the nitrate by repeated evaporations with small quantities of nitric acid.

The volatile organic acids were determined by decomposing the green in a flask containing an acid potassium sulphate solution. The apparatus is as the following figure shows.



[1] This Journal, 23, 485.

In B is placed an excess of potassium bisulphate. Steam free from carbon dioxide is passed into the apparatus till the distillate is neutral to phenolphthalein. The steam is then turned off, the sample inserted in B and the distillation continued till the distillate is neutral. Burners under B and C keep the condensation from accumulating in excessive quantity in the flasks. The flask C serves as a trap to retain traces of bisulphate, copper and arsenic. The distillate caught in E was titrated in the usual manner. Several determinations with zinc acetate gave results in accordance with the theory to the second decimal in percentages. The distillate from samples containing arsenious acid showed, in some cases, a faint trace of arsenic which, however, showed practically no acid reaction with phenolphthalein.

The greatest difficulty encountered in the work, and the only cause of uncertainty in the mind of the writer as to the accuracy of the conclusions, is the difficulty in distinguishing between mixtures and true compounds and in preparing the latter, since this class of bodies does not admit of purification by recrystallization. The microscope gives the most satisfactory evidence of the presence or absence of impurities. Free white arsenic and Scheele's green could be readily detected, even when present in minute quantities. The microscopic examination of Paris green is given very fully and clearly by Sattler.[1]

Samples of the green were made in nearly every possible way and several hundred were analyzed. Only such methods of preparation and such analytical data as seem to have a definite bearing on the problem at hand will be given in this paper.

Formic Green.—Formic acid was treated with freshly precipitated copper hydroxide in excess and filtered. The copper present in solution per cubic centimeter was determined. White arsenic was dissolved in sodium hydroxide by boiling, a drop of phenolphthalein added and dilute formic acid added drop by drop till the color was just discharged. The hot solutions of copper and arsenic were mixed in such proportions that 4 molecules of copper oxide were present for 3 molecules of arsenious oxide. The precipitate of Scheele's green was allowed to stand several days till converted into the characteristic brilliant green precipitate. The composition of this precipitate was as follows:

[1] Z. angew. Chem. 1, 35–47. (Not Z. anal. Chem. 11, 35, as given in Chem. News, 80, 261, and Stillman's "Engineering Chemistry," p. 422; Chem. Pub. Co., 1900.)

	Calculated for $3CuAs_2O_4.CuC_2H_2O_4$. Per cent.	Found. Per cent.
CuO	32.28	32.56
As_2O_3	60.22	59.78
Formic anhydride	7.50	7.70

Acetic Green.—A sample prepared in the same manner as the formic, using acetic instead of formic acid, showed the following composition:

	Calculated for $3CuAs_2O_4.CuC_4H_6O_4$.	Found. Per cent.
CuO	31.39	31.75
As_2O_3	58.55	57.55
Acetic anhydride	10.06	10.31

A very large number of samples of acetic green, made in many different ways, with excess of copper, excess of acetic acid, excess of arsenic, or with an excess of any two of these, showed the presence of 57.3 to 57.7 per cent. of arsenious oxide. The highest result obtained on any sample that appeared free from uncombined white arsenic when examined under the microscope was 58.19 per cent.

Propionic Green.—I find no mention of this compound in the literature of the subject. In preparing it the method used in making the formic green was followed, except that an aqueous solution of white arsenic was used. The green formed was found to be impure under the microscope. Hence it was digested, first with an aqueous solution of white arsenic, then with a solution of sodium propionate. After this treatment all foreign substances seemed to be removed. The analysis gave:

	Calculated for $3CuAs_2O_4.CuC_3H_{10}O_3$. Per cent.	Found. Per cent.
CuO	30.54	30.37
As_2O_3	56.98	56.66
Propionic anhydride	12.48	12.91

Butyric Green.—This green was made in the same manner as the formic green. The analysis gave:

	Calculated for		Analysis given by Wöhler.[1] Per cent.	Found. Per cent.
	$3CuAs_2O_4.CuC_5H_{10}O_4$. Per cent.	$2CuAs_2O_4.CuC_5H_{10}O_4$. Per cent.		
CuO	29.74	30.11	30.5	29.55
As_2O_3	55.49	49.93	50.1	54.00
Butyric anhydride	14.77	19.96	19.4	16.33

[1] Ann. 94, 45.

While fully appreciating the difficulties of obtaining pure substances and the limits of analytical accuracy, these analyses seem to point clearly to the following:

Paris green and its homologues are compounds of copper meta-arsenite and a copper salt of the corresponding acid. The ratio most frequently approaches 3:1 but in some cases approaches 2:1. The crystalline structure within these limits and the color do not vary with the composition. Efforts to obtain compounds approaching the ratio of 4:1 or 1:1 were without result, as will be given later in this paper.

To study the effect of the nature of acids in determining the ratio of the copper arsenite and the copper organic salt, solutions of copper formate, acetate and propionate were so made up that the same quantities of copper were present in equal volumes (2.4683 grams CuO in 132 cc.). Exactly the same amount of sodium arsenite (see method of preparing formic green) was added in each case, and like conditions of temperature were maintained. The arsenic trioxide in each was as follows:

	Calculated for $3CuAs_2O_4 Cu(acid)_2$. Per cent.	Found. Per cent.	Variation.
Formic	60.22	59.23	—0.99
Acetic	58.55	57.47	—1.08
Propionic	56.98	54.77	—2.21

It will be noted that all the figures for the arsenic are below the theory required for 3 of copper arsenite to 1 of copper organic salt, and that the propionic shows a rapid approach towards the ratio of 2:1 as Wöhler found in the butyric. In the same series of acids the stronger the organic acid the more nearly the ratio approaches 3:1. The rule holds true also in the chloracetic acid series which readily form greens.

	Calculated for As_2O_3. Per cent.	Found. Per cent.	Variation.
Trichloracetic	48.64	47.27	—1.37
Monochloracetic	54.83	52.96	—1.87

Green Containing a Dibasic Acid.—All suggestions for structural formulas for Paris green that I am familiar with assume a more or less complicated chain with copper-linking arsenious complexes, terminating with a copper atom at each end, one of whose bonds is saturated with acetic acid. Since, however, acetic acid may be replaced by succinic, such a configuration becomes

improbable, since it involves the conception of a very complicated closed chain. The succinic green was prepared as the formic, and was found to contain 57.20 per cent. of arsenious oxide while the ratio of 3:1 would require 58.60 per cent.

In this connection it may be noted that apparently compounds of the type of Paris green may be formed whenever an acid containing a carboxyl group yields a soluble copper salt and forms no complex ions with copper. I have not succeeded in forming greens under other conditions, though numerous attempts were made.

The Action of Various Solutions on Paris Green.—When Paris green of a composition approximately 3:1 is boiled with a solution of arsenious acid in very large excess, if the green be filtered off and dried, a product of more nearly exactly 3:1 in composition is obtained, but I have never been able to obtain a product having the physical properties of Paris green in which the percentage of arsenic trioxide was as high as 58.55 per cent. as the theory for 3:1 requires. If, however, the boiling be continued the green will suddenly become lighter colored and finally change to a blue-green-white product. By repeated treatment with boiling arsenious acid solution the green is converted into copper meta-arsenite.

	Analysis of sample. Per cent.	Calculated for $CuAs_2O_4$. Per cent.
As_2O_3	71.55	71.33
CuO	28.59	28.67

This copper meta-arsenite was pseudomorphic after Paris green. I find no mention of anhydrous copper meta-arsenite in the literature of the subject. The same substance partially hydrated[1] can be made by treating copper hydroxide with an excess of a solution of arsenious acid, allowing to stand for several days, repeating the process and finally boiling for several hours.

ANALYSIS.

	Per cent.
CuO	28.30
As_2O_3	70.13
H_2O	1.57

The color is identical with the preceding. The substance is a gray crystalline powder. I was unable to combine copper meta-arsenite directly with copper acetate to form Paris green.

[1] Compare Stavenhagen: J. pr. Chem. [2] 51, 1.

By treating Paris green with a neutral solution of copper acetate a brown amorphous powder, pseudomorphic after Paris green, is formed. It contains a higher percentage of copper and a lower percentage of the other constituents than Paris green and is always hydrated. By boiling Paris green with dilute acetic acid the green is slowly dissolved but no marked change in the composition of the undissolved part is to be detected.

Action of Water on Paris Green.—This action is of great practical interest, since soluble arsenic used as an insecticide burns foliage. Notwithstanding the work of several investigators[1] on the subject, Bulletin 151 of the California Experiment Station, p. 19, contains the following paragraph: "Examination by this Station's Laboratory Method.—This takes into account not only the limits of orchard practice with Paris green, but also reckons with the remarkable (?) properties ascribed to Paris green by some chemists when it is treated with plain distilled water; regardless of the fact that this article—acetarsenite of copper—as manufactured to-day, is instantaneously precipitated from complex solutions containing alkali and often excessive quantities of various acids."

A sample of apparently very pure green (composition nearly in the ratio 3:1) was finely pulverized and heated with five hundred parts of distilled water in a sealed tube. Of the original sample there passed into solution,

	Per cent.
CuO	6.46
As_2O_3	24.32
Acetic anhydride	9.27

A sample of the same was boiled for several hours with repeated changes of ammonia-free, carbonic acid-free distilled water. The undissolved portion was finally dried. It showed the following composition:

	Per cent.
Free CuO, not dissolved by cold dilute H_2SO_4	1.48
Combined CuO	49.35
As_2O_3	25.65
Water of hydration and traces of combined acetic acid not determined	.....

These figures seem to point out that "plain distilled water" in sufficient quantity would ultimately resolve Paris green into its component parts.

[1] Haywood: This Journal, **22**, 705; Hilgard: Ibid. **22**, 690; Avery and Beans: Ibid. **23**, 111.

Attempts to Prepare Compounds Analogous to Paris Green Substituting Other Metals for Copper.—As much light had been thrown on the constitution of Paris green by the substitution of other acids for acetic, I endeavored to make similar compounds, using nickel, cobalt, cadmium and zinc in the place of copper. Only zinc gave definite crystalline products.

A solution of zinc acetate containing a little free acetic acid on the addition of an aqueous solution of arsenious oxide deposits a granular white powder, which, under the microscope, appears exactly like certain forms of Paris green except that the balls are white or colorless. The balls are frequently rougher than Paris green balls and the component parts are more easily seen. The individuals appear often in the form of figures g, g_2, h_1, i_1, i_2 as given by Sattler.[1]

The composition of one sample was as follows:

	Calculated for $ZnAs_2O_4$. Per cent.	Found. Per cent.
ZnO	29.13	29.10
As_2O_3	70.87	70.13
Acetic anhydride	.....	0.75

Other samples showed as low a percentage of arsenic as 69.5 per cent., from which a higher percentage of acetic is to be inferred. The products, in my opinion, were zinc meta-arsenite crystallized in isomorphic mixtures with zinc acetate and in which the latter was present in small quantities. Zinc meta-arsenite, of which I find no mention in the literature of the subject, can be readily made by dissolving arsenious acid in sodium hydroxide, adding a drop of phenolphthalein, decolorizing with a little dilute sulphuric acid and adding to a hot solution of zinc sulphate. The crystals are of the form just described.

ANALYSIS OF SAMPLE.

	Per cent.
ZnO	28.95
As_2O_3	70.91

The precipitate was free from sulphates.

When zinc butyrate is substituted for zinc acetate and butyric for acetic acid, the precipitate formed by adding arsenious acid may contain as high as 10 per cent. butyric anhydride. In such cases, however, the precipitate is largely mixed with zinc ortho-

[1] Z. angew. Chem. 1, 37.

arsenite.[1] This higher percentage of the fatty acid, however, shows that butyric acid has a stronger tendency to replace arsenious acid in the zinc as well as in the copper compounds.

In conclusion, I would express my obligations to F. O. Woodruff for his carefully prepared bibliography which he placed at my disposal and to R. Corr and Fred Upson, of this laboratory, without whose careful work in preparing and analyzing compounds, only a small part of which are given here, this work could not have been brought to completion.

THE UNIVERSITY OF NEBRASKA.

A NEW ANALYSIS OF THE WATER OF OWENS LAKE, CALIFORNIA.

BY C. H. STONE AND F. M. EATON.

Received June 30, 1906.

IN the eastern part of California between the White Mountain and Sierra Nevada Ranges, is a V-shaped depression, known as Owens Valley. Measured from crest to crest of the confining mountains, the valley is 10 to 25 miles wide and 125 miles long. The lowest part of the depression is occupied by a saline body of water called Owens Lake. This was originally described as having an area of about 110 square miles, with an average depth of 9 feet 10 inches. The only forms of life inhabiting the water are infusoria, alkali shrimps and the larvae of the alkali flies. There is no outlet, but the lake is fed by the Owens River and a number of small streams, practically all of which enter the valley from the Sierra side. While in the earlier reports it was stated that the loss by evaporation was very nearly counterbalanced by the inflowing water, evidences are abundant to-day that the size of the lake is decreasing. Mr. W. T. Lee, geologist of the U. S. Geological Survey, says in one of his recent bulletins: "The density of the water has increased to a point where sodium bicarbonate precipitates during the winter months without concentration by evaporation. From 1884 to 1894, the lake surface remained practically stationary; from 1894 to 1904 the surface has lowered 16 feet, decreasing the length of the lake by five miles and the width by about two miles."

Owens Lake is probably the largest natural soda deposit in the world. Thirty years ago, Loew estimated that it contained

[1] Bloxam: J. Chem. Soc. 15, 296 (1862).

22,000,000 tons of sodium carbonate. For the past twenty years, the Inyo Development Co. has had an extensive plant for the recovery of this soda at Keeler, so that the conditions have been under careful scrutiny for a long time. From time to time, partial analyses of this water have been made. A few are given below for comparison with our own work. To render such comparison easier they have all been recalculated into parts per million of the various ions. In so far as we know, all have been corrected for the specific gravity of the water.

ANALYSES OF THE WATER OF OWENS LAKE, CALIFORNIA.

	Parts per million.			
	A.	B.	C.	D.
Si	76.5	96.8	984.0	
Fe		9.2		
Al	trace	12.0		
Ca	trace	13.2		
Mg	trace	4.7		
K	2750.6	1548.0	1238.9	
Na	21652.1	26835.6	39032.4	83133.6
Li	trace			
SO_4	9361.7	7066.7	9525.3	20572.4
Cl	13443.8	18214.3	25513.9	56090.0
CO_3	13145.8	18265.2	23573.9	52465.5
PO_4	trace			
B_4O_7	trace	345.6		4590.2
H		59.3		202.0
NO_3	trace			
Organic matter	trace		242.2	
Total solids	60430.	72471.	100111.	217054.
Sp. gr	1.051	1.062[1]		1.1861

"A."—Analysis by Oscar Loew, in 1876. See U. S. G. S. 8th Annual Report, page 295.

"B."—Analysis by T. M. Chatard, U. S. G. S., Bulletin 60. Samples taken September 17, 1886.

"C."—See "Saline Deposits of California," State Mining Bureau Bulletin, No. 24, 1902, page 95.

"D."—Analysis by N. Wrinkle, Manager of the Inyo Development Company's Works, at Keeler, Cal. Sample taken July, 1904.

The sample which we analyzed was collected by Mr. N. Wrinkle, superintendent of the Inyo Development Co., about 2,000 feet from the shore of the lake and at a depth of about 5 feet. As the

[1] At 25° C.

methods applied were necessarily different from those ordinarily used in water analysis, we have thought that a short description of them might be of interest.

Considering the small amounts of calcium, magnesium, phosphates, etc., shown in the above analyses, one's first thought naturally is that a large amount of the water must be evaporated in order to obtain enough of these substances to work with. But a second thought will show the futility of this for the water is already saturated and the evaporation of a large quantity is not only a difficult matter on account of the crust which forms over the surface of the liquid almost as soon as the dish touches the steam-bath, but also undesirable because of the enormous amount of salt to be handled. Therefore it was found desirable to follow the procedure of Mr. T. M. Chatard in his excellent study of this lake in 1886, and work on portions of 50 cc. to 100 cc. The specific gravity was found by the pycnometer method, each of us making the determination independently and arriving at identically the same result.

The question of total soluble salts was a troublesome one on account of the amount of water, both mechanically held and chemically combined, which must be expelled without driving off carbon dioxide. Being unable to secure an apparatus such as Chatard used we were obliged to devise a method of our own. Ten cc. of the water were evaporated to dryness in each of two platinum dishes; one of these was ignited at a low heat, weighed and the carbon dioxide in the residue determined gravimetrically. In the other, carbon dioxide was determined without previous ignition. Then having determined the carbon dioxide in the original water, it was easy to calculate the loss of the same due to evaporation and ignition. From these data the weight of the total solids with all water expelled may be derived.

We realize that this makes no allowance for organic matter, but this is negligible when compared with the weight of the solids found.

Another portion of 100 cc. was acidified, evaporated to dryness, and the silica dehydrated, filtered off and weighed. In the filtrate the iron and the alumina were precipitated by ammonia, but on account of the presence of phosphates it seemed probable that these phosphates and also calcium would be found in the

precipitate. Therefore we fused the latter with potassium acid sulphate and after solution determined the phosphoric acid, and tested for calcium with negative results. Deducting the weight of the phosphoric acid from the total weight of precipitate gave us the weight of the iron and alumina. In the filtrate from the ammonia precipitation the lime and magnesia were determined as usual.

In two other portions of 50 cc. each sulphuric acid was determined as barium sulphate and in the filtrate from this the total alkalies were determined in the usual way, using milk of lime and ammonium carbonate. In one of these the potash was determined with chlorplatinic acid. From the other, lithium was extracted with amyl alcohol according to the method of Gooch and Whitfield (Bull. 47, U. S. G. S.). Two such separations were made in order to insure the complete extraction of the lithium and the proper correction was applied for the volume of amyl alcohol used. The lithium was then converted to sulphate and weighed. This residue contained whatever rubidium, caesium and thallium were present in the water and qualitative tests were made for these according to methods given in Behren's "Microchemical Analysis." Phosphoric acid was determined in a separate portion of 50 cc. by precipitation with ammonium molybdate and finally with magnesia mixture, having first removed the arsenic with hydrogen sulphide. Carbon dioxide and chlorine were determined gravimetrically, the one by absorption in caustic potash and the other by precipitation with sliver nitrate.

We first endeavored to determine nitrates by the Sprengel method, having previously removed the chlorine with silver oxide, but found on adding the phenolsulphonic acid that red fumes of nitrous oxide were freely evolved. In view of the large amount of nitrate present we were obliged to resort to another method. Twenty-five cc. of the water were diluted to 200 cc., 10 cc. of caustic soda added and the solution boiled until the volume was reduced to 70 cc. When cold, it was poured into a glass cylinder holding 120 cc., 20 sq. cm. of aluminum foil added and the mouth of the cylinder closed with a cork bearing a small tube filled with pumice moistened with hydrochloric acid. After standing several hours, the contents of the tube were transferred to a retort, caustic potash added and the ammonia distilled off and determined by titration.

Without expecting any particular results, hydrogen sulphide was passed into a portion of the water heated to boiling. To our surprise, a considerable yellow precipitate formed, and on examining this by the Marsh test it was found to be arsenic. This was then determined quantitatively in 100 cc. of the water by precipitation with hydrogen sulphide and finally with magnesia mixture. Every reagent used was tested for arsenic and several blanks were run, so that there is no reasonable room for doubt that the arsenic came from the water itself.

After attempting to determine the boric acid by the methods of Marignac and of Gooch, and having poor success with the former on account of the amount of salt in the water, and with the latter because of the difficulty in removing the chlorine, we finally adopted the following method: 100 cc. of the water were placed in a large Florence flask with 300–400 cc. of distilled water, the boric acid liberated by hydrochloric acid and then the flask was connected to a condenser and steam blown through it. In this way the boric acid was distilled over with the steam free from everything but hydrochloric acid and was received in a solution of caustic potash. A test made at the end of the operation showed that all the boric acid had passed over into the potash solution. Now the solution in the receiver, containing only potassium borate, potassium chloride and potassium hydroxide, was treated exactly as in Stromeyer's process save that Fresenius' modification for removing the silica was adopted.

The results of the analysis are given in the following table; all are expressed in parts per million, and are corrected for the specific gravity of the water.

Duplicates were run on all the determinations except lithium and boron, and the results checking very closely in all cases, they have been averaged for this table. The iron and alumina were calculated as alumina because of the small amount of the precipitate which seemed to be iron. The bicarbonates were determined by titration with sodium acid sulphate and found to be 7721 parts, calculated as HCO_3.

OWENS LAKE.
Averages.

Specific gravity	1.1954
Si	139.2
FeAl (calculated all as Al)	47.5
Ca	33.8
Mg	14.9
K	3447.9
Na	81176.3
Li	56.8
SO_4	21173.5
Cl	52898.0
CO_3	52325.5
PO_4	237.9
B_4O_7	296.4
H	130.2
As	83.8
NO_3	947.7
Rb	trace
Cs	trace
Total solids (by addition)	213320.
Total solids determined	213661.
O_2 (for SiO_3, Al_2O_3 and As_2O_3)	310.3

As will be seen from the table, sodium and potassium carbonates, chlorides and sulphates constitute by far the major part of the salts present in the water. The large amount of sulphate is important because this is the most troublesome salt to a manufacturer of soda. The arsenic is a curious and rather unexpected feature, for while it is often present in ground waters it is, we believe, seldom a constituent of surface waters. In this case it very probably arises from the decomposition of arsenopyrite. The amount of phosphate is another interesting feature; in previous analyses of water of the lake this has been reported simply as trace and in the majority of water analyses it is not determined at all. There are, we believe, few water analyses on record where the amount of phosphate reported is as great as in Owens Lake. Another noteworthy determination is that of nitrates. Of course the amount here reported may be exceeded in a few cases where the water percolates through nitrate beds, but this figure has rarely if ever been reached by a surface water. The carbonate is the feature of greatest commercial interest and is the largest we have ever found in a natural water, being over three times the amount present in the Big Soda Lake at Ragtown,

Nevada. It may be of interest to compare the chlorine found in Owens Lake with that present in various other saline waters. The average chlorine for the ocean is about 1900 parts per 1,000,000; Big Soda Lake has 40,000 parts; Great Salt Lake (in 1873) 73,000; Urmiah Lake, 120,000; Bogdo Lake, 160,000; Indevsk Lake, 160,000; Elton Lake, 170,000; the Dead Sea, in 1864, a maximum of 170,000; and two salt springs in Oklahoma, recently examined by one of us, over 180,000 parts. Thus it will be seen that all the above-named waters, with the exception of the ocean and Big Soda Lake, have a higher chlorine content than Owens Lake, and exactly the same relation holds with regard to the total solids.

While no general conclusions can be drawn from the results of a single analysis, this one has at least shown that the water of Owens Lake is rapidly concentrating and at the present rate will soon reach the saturation point. It has also demonstrated the existence in determinable quantities of certain substances which have hitherto been neglected. We believe that if a similar analysis could be made, at regular intervals, of several of the important saline bodies of water, such as Great Salt Lake, Owens Lake, Soda Lake, etc., interesting and valuable data would be accumulated, and it is our hope to be able to undertake a small portion of such work in the near future.

U. S. GEOLOGICAL SURVEY,
BERKELEY, CAL.

[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL AND PHYSIOLOGICAL EXAMINATION OF THE FRUIT OF CHAILLETIA TOXICARIA.[1]

(A WEST AFRICAN POISON.)

BY FREDERICK B. POWER AND FRANK TUTIN.

Received June 19, 1906.

THE present investigation of the fruit of *Chailletia toxicaria*, Don, was undertaken at the suggestion of Dr. W. Renner, Medical Officer, Colonial Hospital, Freetown, Sierra Leone, who also kindly provided us with the material for this purpose.

The interest which this subject possesses will be apparent from

[1] Presented, in abstract, at the International Congress of Applied Chemistry, Rome, Italy, April, 1906.

the following abstract of a paper published by Dr. Renner, entitled "Native Poison, West Africa."[1]

"For some years now, death by poison has been the subject of talk in the Colony of Sierra Leone, and one could scarcely credit the statements so often made with respect to this subject. No one, it would appear, dies from natural causes. Poisoning in one form or another is put down as the cause of death, not only among the poor but also among the rich, and yet no one would or could come forward to attest the fact that such a one had been poisoned by such a substance. Some of these deaths which appear to be mysterious have given cause for great alarm and anxiety, and aroused a feeling of dread and bitterness against the country doctors to whom they are attributed.

"A peculiar kind of disease, of the origin of which no account could be given, is now and again met with among the people. The European doctor, when called in, is puzzled, for he sees before him a young healthy man or woman, between the ages of twenty-three and forty years, struck down with paralysis. He examines the case carefully, cross-examines scrupulously the patient and his friends, and fails to arrive at any conclusion from these as to the source of the trouble. He suspects poison, and is told that the person has been poisoned. He endeavors to treat the symptoms, and either fails or the case is removed to a country doctor. The individual may recover or die, this depending on the nature and the quantity of the poison administered. These cases are brought forward daily. It has been my fortune lately to discover the cause of one of the mysterious and sudden diseases that affects the natives in the form of paralysis of the lower limbs."

A description is given by Dr. Renner of a case of poisoning, which occurred with a native laborer through his having eaten some fish on which the ground fruit of *Chailletia toxicaria* had been strewn for the purpose of killing rats, and the article then continues as follows:

"The *Chailletia toxicaria* belongs to the natural order of *Chailletiaceæ*, and is known as 'Ratsbane.' In the Colony proper it is called 'Broken Back.' By the Mendis of the Hinterland it is known under the name of 'Magbevi,' and by the Timnes as

[1] J. African Society, 1904, pp. 109–111. Compare also The British Medical Journal, June 4, 1904, p. 1314.

'Manăk.' It grows plentifully in West Africa and South America, and the fruit, which contains the poisonous substance, is used largely for the destruction of rats and other animals; but beyond this it is also used extensively by the people in the Colony and the Hinterland to poison one another. Conversing with some of the older men of the Timnes and Mendis, I found that with them it is very frequently used against their enemies to poison well-water or streams which supply hostile villages. Domestic animals poisoned by it are seen to rush about in great excitement as if in severe pain; they vomit, and drag their hind limbs, which ultimately become paralyzed. The forearm and chest muscles become paralyzed also, and they die from paralysis of the respiratory centre."

In the "Flora of Tropical Africa," by Daniel Oliver, F.R.S., London, 1868, Vol. I, p. 341, a complete description is given of the plant in question, from which the following, including references to its synonymy and habitat, is abstracted:

"*Chailletia toxicaria*, Don, DC. Prod. II, 57. A glabrous shrub or the young shoots and inflorescence mealy-puberulous at first. Leaves rather coriaceous ..... 2½–6 inches long, 1¼–2¼ inches broad, occasionally rather larger. Fruit 1–1½ inches long, ellipsoidal, hard and woody, one-celled, one-seeded.

"*Synonym.*—*C. affinis*, Planch. Fl. Nigrit 276.

"*Habitat.*—Upper Guinea, Sierra Leone, and Senegambia."

The "Treasury of Botany," by Lindley and Moore, London, 1899, Vol. I, p. 260, also gives a description of *Chailletia*, together with the following information:

"A genus which is found more or less in most tropical countries, but represented in greatest numbers in Brazil. The only extra-tropical species is *C. cymosa*, which is a native of South Africa; and the only species whose uses are recorded is *C. toxicaria*, a native of Sierra Leone, where the seeds of this plant are said to be used by the colonists for poisoning rats and by them called rats-bane. Upwards of thirty species are known."

The above-mentioned *Chailletia cymosa* is of special interest in this connection, as will be evident from the following notice of it recorded in the "Bulletin of the Imperial Institute," 1903, Vol. I, p. 14. "Preliminary experiments have shown that the leaves furnish prussic acid when powdered and moistened with

water, and from them a cyanogenetic glucoside has been isolated, and is being further examined."

A description of this species of *Chailletia* is given in the "Flora Capensis," by Harvey and Sonder, Dublin, 1859–1860, Vol. I, p. 450, from which the following is abstracted:

"*Chailletia cymosa* (Hook. *Ic. Pl.* t. 591). Habitat, Aapges River, Burke and Zeyher! Oct. (Herb. Hook., T. C. D.). A very dwarf shrub or suffrutex, under a foot in height. Leaves 3–3½ inches long, 6–10 lines wide, etc. Fruit unknown. A remarkable plant, very different in habit from others of the genus, but apparently not differing generically, unless the fruit afford a character."

Experimental.

The material received by us from Dr. Renner, of Sierra Leone, corresponded with the description of the fruit of *Chailletia toxicaria*, Don, as recorded in Oliver's "Flora of Tropical Africa,"[1] with the exception that it is occasionally two-celled and two-seeded. This is also the case with authentic specimens of these fruits in the Museum of Economic Botany at Kew. The weight of the individual dry fruits ranges from about 5 to 8 grams.

The following preliminary experiments were conducted.

Test for Alkaloid.—Ten grams of the powdered fruit were digested with Prollius' fluid, and the resulting liquid filtered and evaporated. The residue, extracted with acidulated water, afforded no reaction with the usual alkaloid reagents.

Test for a Cyanogenetic Glucoside.—As it has been observed by other investigators[1] that the leaves of *Chailletia cymosa* contain a cyanogenetic glucoside, the fruit of *C. toxicaria* was specially tested for a substance of this class. Ten grams of the ground fruit were mixed with a little water and allowed to stand in a tightly corked flask for about twenty-four hours. As no odor of hydrocyanic acid was then apparent, an emulsion of sweet almonds was added, but this produced no evident change. The liquid was finally distilled, and the complete absence of hydrocyanic acid in the distillate was established by chemical tests. It could, therefore, be concluded that the fruit of *Chailletia toxicaria* does not contain a cyanogenetic compound, and this conclusion was confirmed by the more complete examination of

[1] Loc. cit.

a very much larger quantity of the fruit, which will subsequently be described.

Test for a Poisonous Proteid.—It was considered possible that the poisonous action of the fruit might be due to a proteid substance, such, for example, as ricin, abrin or robin. Fifty grams of the ground fruit were therefore digested with water at the ordinary temperature for three days, when the mixture was brought upon a strainer, expressed, and the liquid filtered. The clear filtrate afforded, however, no reaction for a soluble proteid.

Extraction with Solvents.—In order to obtain some further preliminary information respecting the character of the drug, 100 grams of it, in fine powder, were extracted successively in a Soxhlet apparatus with various solvents. The amounts of extract obtained, after drying in a steam-oven until of constant weight, were as follows:

		Per cent.
Petroleum (b. p. 40–60°)	extracted	2.00
Ether	"	0.26
Chloroform	"	1.10
Ethyl acetate	"	3.04
Alcohol	"	6.84
	Total,	12.24

For the purpose of a systematic examination of the constituents of the *Chailletia* fruit, 3000 grams of it, ground to a fine powder, were first extracted in a percolator with cold light petroleum, and subsequently with hot alcohol.

A. EXAMINATION OF THE PETROLEUM EXTRACT.

This was a yellowish brown fat, which, at ordinary temperatures, consisted of a mixture of an oily substance and a granular solid, but when exposed to cold became almost completely solid. The total amount of fatty matter was 55 grams, corresponding to 1.83 per cent. of the weight of the fruit. The solid was separated from the oil by filtration at the pump, then dissolved in hot acetone, some alcohol added, and the solution allowed to stand for a time. A little fluffy matter first separated, which was removed, and the fat was then deposited in the form of white nodules. These were separated by filtration, washed with alcohol, dried on a tile, then dissolved in a large quantity of absolute alcohol, in which they were sparingly soluble, and the solution filtered. When the liquid was nearly cold, the fat separated in white, crystalline

nodules, which were removed by filtration. After drying on a tile, a portion was finally dried in a vacuum desiccator, when it melted at 42–43°. Another portion was dried by heating in a steam-oven, when, after solidification, it melted at 35–40°. The whole of the substance was then recrystallized from absolute alcohol, when it melted sharply at 43°. Its solution in chloroform readily absorbed bromine.

0.1450 gram gave 0.4072 gram CO_2 and 0.1571 gram H_2O. C = 76.6; H = 12.0; $C_3H_5.(C_{18}H_{35}O_2)_2.C_{18}H_{33}O_2$ requires C = 77.0; H = 12.1 per cent. 0.2499 gram absorbed 0.0686 gram I. Hence the iodine value = 27.5.

This crystalline substance was evidently *oleodistearin*, which has a calculated iodine value of 28.6, and is stated to melt at 44°.[1] Further proof of its identity was afforded by the following experiment: 1.6 grams of the substance were hydrolyzed with an alcoholic solution of potassium hydroxide, and the acids thus obtained were fractionally crystallized many times. The most readily soluble fraction consisted of an oil which was found to be unsaturated, on treatment with nitrous acid formed a solid mass, and therefore consisted of oleic acid. The other fractions melted at 69–70°, and consisted entirely of stearic acid, as shown by the following analysis:

0.1049 gram gave 0.2912 gram CO_2 and 0.1198 gram H_2O. C = 75.7; H = 12.7; $C_{18}H_{36}O_2$ requires C = 76.0; H = 12.7 per cent.

The identification of the mixed triglyceride, oleodistearin, as a constituent of the fatty oil from *Chailletia* fruit is of considerable interest, inasmuch as the number of substances of this class that have been isolated from either vegetable or animal fats and definitely characterized is comparatively small (compare Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats, and Waxes," third edition, Vol. I, p. 14).

The original filtrate from the granular solid which afforded the oleodistearin consisted of a brownish oil, which became partially solid on cold days. This, together with the fatty matter contained in the first and second mother-liquors from the recrystallization of the oleodistearin, was hydrolyzed by boiling with an alcoholic solution of potassium hydroxide. The alcohol was then removed, the alkaline residue mixed with clean sand, dried, and extracted in a Soxhlet apparatus with light petroleum. On

[1] Ber. 32, 388 (1899). Compare also Chem. Centr. 1, 1716 (1905).

removing the petroleum from this extract a dark brown resinous residue was obtained, which was dissolved in much alcohol, and the liquid boiled with animal charcoal and filtered. On cooling, a small quantity (about 0.5 gram) of a substance was deposited in the form of crystalline plates. This was removed by filtration, recrystallized several times from ethyl acetate, and then from ordinary spirit, in which it was very sparingly soluble. It was then almost colorless, and, after drying at 100°, melted at 138–143°. After again crystallizing from spirit, and drying at 100°, when it appeared to lose some water of crystallization, it softened and gradually melted at 135–148°.

0.0854 gram, dried at 100°, gave 0.2630 gram CO_2 and 0.0952 gram H_2O. C = 84.0; H = 12.4; $C_{28}H_{44}O$ requires C = 83.9; H = 11.8 per cent.

This substance was evidently a *phytosterol*, since it also afforded the color reactions characteristic of the latter when dissolved in chloroform and treated with acetic anhydride and sulphuric acid. As the melting-point was not sharp, it was possibly a mixture of substances of that class, but the amount was too small to admit of a further separation.

The alkaline mixture with sand, from which the phytosterol had been extracted, was treated with hot water in order to dissolve the potassium salts, the solution then acidified with sulphuric acid, and distilled in steam. A clear distillate was obtained, containing only a small amount of acids, which, after converting into their barium salts, were found to consist chiefly of *formic acid* with a little *butyric acid*. The non-volatile acids remaining in the flask were removed by shaking the liquid repeatedly with ether. The ethereal liquid was washed with water, dried with calcium chloride, the ether then removed, and the residue dissolved in hot spirit. After as much as possible of the solid acids had been removed by crystallization, the oily acids which separated from the mother-liquors were redissolved in alcohol and completely precipitated as lead salts by the addition of a solution of lead acetate in dilute alcohol. These lead salts were collected on a filter, washed with alcohol, dried, and then extracted with ether, when the greater portion dissolved. From the portion of lead salts which remained undissolved by this treatment the acids were regenerated, and, being solid, they were added to the above-mentioned solid acids which had previously

been separated by crystallization. The whole was then fractionally crystallized, when the most sparingly soluble fractions were found to consist of *stearic acid* (melting-point 69°), while the more readily soluble ones appeared to be a mixture of stearic and palmitic acids, and melted at 53–60°.

From the above-mentioned portion of the lead salts which had been dissolved by ether the acids were likewise regenerated. An oily liquid was thus obtained, a portion of which, when treated with nitrous acid, became converted into a solid mass, thus indicating the presence of *oleic acid*. The remainder of this liquid was distilled under diminished pressure, when a pale yellow oil was obtained, from which no solid matter separated.

0.2508 gram absorbed 0.2696 gram I. Hence the iodine value = 107.5.

As oleic acid has a calculated iodine value of 90.1, it was evidently associated with some acid possessing a higher degree of unsaturation.

B. EXAMINATION OF THE ALCOHOL EXTRACT.

It has already been stated that the *Chailletia* fruit, after having been extracted with light petroleum, was extracted with hot alcohol. This alcoholic extract was concentrated and mixed with water, in order to precipitate the resin. The mixture was warmed to expel the remaining alcohol, allowed to cool, and the insoluble resinous substance removed by filtration, washed with hot water and dried.

I. *The Resin.*—This formed a dry, brown, amorphous powder, having an odor somewhat resembling that of chocolate. The amount of resinous substance was 76 grams, corresponding to 2.5 per cent. of the weight of the fruit. It appeared to be slightly soluble in water, as a further quantity was deposited on concentrating the aqueous liquid. After keeping for some time it lost its original smell, and became much more sparingly soluble in alcohol. In order to ascertain whether any definite substance could be obtained from it, it was mixed with prepared sawdust, and extracted successively in a Soxhlet apparatus with chloroform, ethyl acetate, and alcohol. The amounts of extract obtained by these solvents, after drying in a steam oven, were as follows:

(*a*) *Chloroform Extract*, consisting of a dark green, soft resin, 11.83 grams.

(*b*) *Ethyl Acetate Extract*, a yellowish brown, very sticky resin, 4.30 grams.

(*c*) *Alcohol Extract*, a nearly hard, brown resin, 9.40 grams.

These results showed the resin to consist of a complex mixture, and, as after the final extraction with alcohol about two-thirds of the original substance remained undissolved in the form of a brown powder, it was evident that it had undergone some change, either in drying or in the process of extraction. As there appeared to be nothing crystalline in these products, they were not examined chemically, but were reserved for physiological tests.

II. *The Aqueous Liquid.*—The liquid from which the above-described resinous substances had been separated had a brownish color, gave a black coloration with ferric chloride, a dense, grayish colored precipitate with basic lead acetate, and reduced Fehling's solution. In order to purify it, basic lead acetate was added until no further precipitate was produced. This precipitate was collected by filtration at the pump, washed with a little water, and then suspended in water and decomposed by hydrogen sulphide. The filtrate from the precipitated lead sulphide formed a clear, dark brown liquid, which was concentrated under diminished pressure. A thick, dark brown syrup was thus obtained, which consisted chiefly of tannic and coloring-matters, and deposited nothing crystalline, even after long standing.

The aqueous filtrate from the basic lead acetate precipitate was completely deprived of lead by means of hydrogen sulphide, and then concentrated under diminished pressure to the consistency of a thick syrup. When heated with potassium hydroxide it evolved ammonia, and it readily reduced Fehling's solution. An aqueous solution of the syrup was slightly levorotatory, and afforded an osazone melting at 214°. The sugar, therefore, appeared to be chiefly *i-glucose*, the osazone of which is stated to melt at 217–218°.

PHYSIOLOGICAL TESTS AND ATTEMPTS TO ISOLATE THE POISONOUS PRINCIPLE.

The indefinite character of the products obtained from the original alcoholic extract *B*, as above described, rendered it important at this stage of the investigation that we should ascertain

which of them represented or contained the poisonous principle. For this purpose some physiological experiments were conducted for us, with essentially the following results.

I. *The Resin.* — The three extracts obtained from this by successive treatment with different solvents, as previously described, were separately tested. In each case 0.5 gram of the extract was administered to a small dog.

(*a*) *Chloroform Extract.*—This, after some hours, produced narcosis, and ultimately death, but did not cause the delirium and epileptiform convulsions which are such characteristic features of the poisonous action of *Chailletia* fruit.

(*b*) *Ethyl Acetate Extract.*—This produced the characteristic convulsions, thus differing in its action from the preceding extract.

(*c*) *Alcohol Extract.*—This caused nausea, but no toxic symptoms.

II. *The Aqueous Liquid.*—This liquid, from which the above-mentioned resinous substances had been separated, and which had been further purified by means of basic lead acetate, was found to be highly toxic. When concentrated to a syrupy consistency it amounted to about 200 grams. Of this syrup 0.5 gram was administered to a dog, when after an interval of three hours the characteristic convulsions occurred, which were followed by death within fifteen minutes. The decomposed lead acetate compound was also toxic, and when given in the same amount as the syrup produced a similar effect, although somewhat more slowly. This result, however, was probably due to the occlusion of some of the aqueous liquid with the lead acetate precipitate, as the latter did not permit of being very thoroughly washed.

The preceding physiological experiments having shown that the syrupy aqueous liquid possessed in a high degree the poisonous properties of the *Chailletia* fruit, and as nothing crystalline separated from it, even after standing for several weeks, an attempt was made to isolate the toxic principle by further treatment. The syrup was accordingly mixed with prepared sawdust, the mixture thoroughly dried in a vacuum over sulphuric acid, then brought into a Soxhlet apparatus, and extracted for two days with dry ethyl acetate. This removed a quantity of substance which was only sparingly soluble in the ethyl acetate, for it separated from the hot liquid as a brownish syrup. The liquid

decanted from the latter was concentrated to a small volume, when another portion of syrup separated, which was removed. From the remaining liquid the ethyl acetate was for the most part distilled off, when from the resulting syrup an exceedingly small quantity of a colorless, crystalline substance separated in the form of needles. The syrup containing these needles was diluted with a little alcohol and filtered, and a very small amount of the crystalline substance was thus obtained. This was only sparingly soluble in ethyl acetate and in alcohol, and practically insoluble in water. After recrystallization from hot alcohol, and drying at 100°, it melted at 245–247°, and left no ash on ignition. The amount of this substance was much too small for further chemical examination, but it was found to possess no marked physiological action, and evidently did not represent the toxic principle of the fruit.

The syrup from which the ethyl acetate liquid was first decanted represented the greater part of the substance extracted by this solvent. It readily reduced Fehling's solution, yielded a crystalline osazone melting at 211–212°, and evidently consisted largely of *i*-glucose.

It was subsequently ascertained, by physiological tests, that the syrup which separated from the ethyl acetate extract was devoid of toxic properties. A small portion of the sawdust, containing the substance which had been subjected to prolonged extraction with ethyl acetate, was then extracted with water, and, as this extract still possessed a high degree of toxicity, it was manifest that the ethyl acetate had removed practically none of the poisonous principle.

With consideration of these results, the dried mixture with sawdust was afterwards extracted for one day in a Soxhlet apparatus with absolute alcohol. The liquid in the flask deposited a quantity of syrup, from which the alcohol was decanted, and as from the latter, on further concentration, an additional quantity of syrup separated, this was also removed from the alcoholic liquid. These preparations, together with an aqueous extract of the sawdust remaining in the extraction apparatus, were all physiologically tested. They were all highly toxic, did not differ appreciably in their action, and nothing crystalline could be obtained from them.

The preliminary examination of *Chailletia* fruit having shown

the absence of an alkaloid, and, as so many non-alkaloidal, poisonous substances are glucosides, it was thought probable that the active constituent of the aqueous extract was also a substance of this nature. With the hope of obtaining some confirmation of this view, it was sought to ascertain whether it would yield any definite hydrolytic product. The material contained in the Soxhlet apparatus was, therefore, extracted with water, and in this liquid were dissolved the syrups obtained by the previous extraction with absolute alcohol. The whole was first shaken out several times with ether, which, however, removed only a trace of a brownish, syrupy substance. Sufficient hydrochloric acid was then added to make an approximately 5 per cent. solution, and the mixture boiled for three hours in a flask with an inverted condenser. During the boiling a large quantity of a black amorphous resin separated, and the entire mixture was subsequently distilled in steam. The first drops that passed over were slightly turbid, and had a somewhat empyreumatic odor, but no aldehyde or ketone could be detected in the distillate. The residue in the distilling flask was allowed to cool, and repeatedly shaken with ether. This did not dissolve the black resin, but removed a small quantity of a brownish syrup, which had an unpleasant odor, and, on the addition of water, separated a sticky resin. All the attempts to isolate the toxic principle, or to obtain some definite derivative of it, were, therefore, unsuccessful.

SUMMARY AND CONCLUSIONS.

The results of the investigation of the fruit of *Chailletia toxicaria*, Don, as detailed in the preceding pages, may be briefly summarized as follows:

A preliminary examination showed the fruit to contain no alkaloid, cyanogenetic glucoside, or soluble proteid, to which its highly poisonous properties could be attributed. The possible presence of a cyanogenetic glucoside was particularly considered, in view of the recorded statement that such a substance has been isolated from the leaves of the South African species, *Chailletia cymosa*, Hook.[1]

On extracting 3000 grams of the fruit with light petroleum (boiling-point 40–60°), 53 grams, or 1.83 per cent. of a yellowish

[1] Compare "Bulletin of the Imperial Institute," 1903, Vol. I, p. 14.

brown fat were obtained. From this a quantity of the mixed triglyceride, *oleodistearin*, $C_3H_5.(C_{18}H_{35}O_2)_2.C_{18}H_{33}O_2$, melting-point 43°, was directly separated, and from the residual fatty matter, after hydrolysis with an alcoholic solution of potassium hydroxide, the following substances were isolated: (1) A small quantity of a *phytosterol*, $C_{26}H_{44}O$, or possibly a mixture of substances of this class, melting at 135–148°; (2) *Stearic* and *oleic acids*, the latter being apparently associated with an acid having a higher degree of unsaturation; (3) Very small amounts of *formic* and *butyric acids*.

The alcoholic extract of the fruit which had previously been deprived of fatty matter, when concentrated and mixed with water, yielded a quantity (76 grams) of *resinous substance* corresponding to 2.5 per cent. of the weight of the fruit. This consisted of a complex mixture, from which nothing crystalline could be obtained. By successive extraction with chloroform, ethyl acetate, and alcohol it was, however, resolved into products which differed essentially in their physiological action. The chloroform extract, for example, had a narcotic or paralytic effect, while the ethyl acetate extract produced delirium and convulsions, and the alcohol extract, although causing nausea, was not distinctly toxic.

The aqueous liquid, separated from the above-mentioned resinous substance, and deprived of tannic and coloring-matters, when concentrated under diminished pressure, formed a thick syrup, which contained a large amount of *glucose*. This syrup was extremely poisonous, producing, when administered to a dog in relatively small doses, the characteristic action of the fruit, *viz.*, delirium and epileptiform convulsions, soon followed by death. Although many attempts were made to separate the poisonous principle from the syrup by extracting the latter with various solvents, such as ethyl acetate, absolute alcohol, etc., these were unsuccessful, as all the liquids which were capable of removing the active principle also dissolved considerable amounts of sugar.

The physiological experiments connected with this investigation have led to the observation that, with the lower animals, the effects of the poison contained in the *Chailletia* fruit are only manifested some time after its ingestion. According to the amount administered, a period of several hours may elapse before

the occurrence of the characteristic convulsions, but, after the onset of the symptoms, death usually follows within fifteen to thirty minutes. A *post-mortem* examination of the animal shows a condition of cerebral congestion and thrombosis of the superior longitudinal sinus.

It was considered possible that the narcotic effects produced by the chloroform extract of the resin, and the delirium and convulsions caused by the aqueous extract, as above described, are due to the same substance, and that the difference in the symptoms may depend upon the amount of the poison administered or the rate of its absorption. In order to test this assumption successive sub-toxic doses were given to a small dog during a period of several days. Nothing of a definite nature occurred until the tenth day, when the characteristic delirium commenced, followed shortly by convulsions, and death then ensued within about one hour. The *post-mortem* examination showed a condition of cerebral congestion, and a small patch, apparently of cortical necrosis, near the right crucial sulcus. These experiments thus permit of the following deductions:

(1) That the fruit of *Chailletia toxicaria* contains at least two active principles, one of which causes cerebral depression or narcosis, and the other cerebral excitation, leading to epileptiform convulsions.

(2) That the poison which causes convulsions is very slowly excreted, so that a cumulative effect is produced by the administration of a series of individually innocuous doses.

It may finally be stated that all the physiological experiments required in the course of this investigation were conducted in the Wellcome Physiological Research Laboratories by Mr. H. H. Dale, and our best thanks are due to him for the valuable assistance he has given us.

ON THE ACTION OF ACID CHLORIDES ON MIXTURES OF AMINES.

By F. B. Dains.

Received July 5, 1906.

In the course of an investigation on the action of acid chlorides on ureas of the type RNHCSNHR′, the question arose, which an effort was made to answer, whether when a mixture of two

amines was treated with an acid chloride, any preference would be shown as to the amine attacked, and if so what the conditions were that would govern it. Thus given a molecular mixture of two amines and an acid chloride, there might be obtained as products, first the acyl derivatives of the two amines plus the hydrochlorides of the two amino bodies, and second the acyl derivative of one amine plus the salt of the other, a condition which can be represented as follows:

$$XNH_2 + YNH_2 + RCOCl = XNHCOR + YNHCOR + XNH_2HCl + YNH_2HCl \text{ or } XNHCOR + YNH_2HCl.$$

The results thus far obtained in this investigation point to the general conclusion, that when there is any appreciable difference in basicity between the two amines, there will be formed largely or altogether the acyl derivative of the more negative amine and the salt of the more positive one.

$$\text{Pos. } NH_2 + \text{Neg. } NH_2 + RCOCl = \text{Neg. } NHCOR + \text{Pos. } NH_2HCl.$$

The terms positive and negative are used in a somewhat restricted sense, referring only to the ease of replacement of the hydrogen atom, since the results from this standpoint may not always agree with those obtained in other ways. Thus from the measurement of the electrical conductivity monoethylamine is a stronger base than ammonia, yet it is found that an amino hydrogen atom of ethylamine is more easily replaced than the hydrogen atom of ammonia.

EXPERIMENTAL.

The experimental work was done under two general conditions, either dissolving molecular quantities of the two amines in a neutral solvent like benzene or ether, and then adding the acid chloride either alone or diluted with the same solvent; or suspending the amines in a relatively large volume of water and then adding the acid chloride as in the usual Baumann-Schotten reaction.

Without making quantitative measurements, it seemed as if the reaction proceeded more rapidly and smoothly under these conditions than when caustic soda was used to combine with the hydrochloric acid set free. In the majority of cases the hard granular acyl derivative formed almost immediately, while the hydrochloride of the amine remained in solution when water was used.

Ammonia and Primary Amines.—Ammonia, if not in too great excess, can be used to combine with the free acid in the formation of benzoyl derivatives of primary amines giving a smooth and rapid reaction.

Ammonia and Ethylamine.—One molecule of ammonia and one molecule of monoethylamine were dissolved in an excess of water and one molecule of benzoyl chloride added with shaking. An oil was formed which was very soluble in alcohol and which, on standing, slowly solidified to long needles of ethylbenzamide (melting-point 67°). The solution contained ammonium chloride.

Ammonia and Aniline.—Benzoyl chloride gave, with molecular proportions of ammonia and aniline, a hard granular precipitate of benzanilide, and ammonium chloride.

Ammonia and o-Toluidine.—These amines gave, in water solution with benzoyl chloride, easily and smoothly *o*-benztoluide and ammonium chloride.

Ammonia and m-Brom-p-toluidine yielded under the above conditions ammonium chloride and benzoic *m*-brom-*p*-toluide.

Ammonia and Phenylhydrazine.—Benzoyl chloride was added to the above amines in water solution. The substances reacted quickly and on examining the products formed, there were discovered ammonium chloride, phenylhydrazine, and dibenzoylphenylhydrazine. The course of the reaction can be represented as follows:

$$2NH_3 + 2C_6H_5NHNH_2 + C_6H_5COCl = 2NH_4Cl + C_6H_5NHNH_2 + C_6H_5N(COC_6H_5)NHCOC_6H_5.$$

The first action of the acid chloride is to form the monobenzoylphenylhydrazine, but as this has still a second replaceable hydrogen atom and is more negative than either the ammonia or the phenylhydrazine, this hydrogen atom is substituted by the second benzoyl group giving the dibenzoylphenylhydrazine.

Aniline and Other Primary Amines.—Aniline, the simplest of the aromatic amines, affords a convenient standard of comparison in its reactivity with other amino bodies as to their relative positive or negative nature. Thus, where the second amine is more positive the products are an acyl anilide and the salt of the second amine. This has already been shown to be the case with ammonia and aniline.

Aniline and Ethylamine. — With molecular proportions of

ammonia, ethylamine and benzoyl chloride in water solution, the products were ethylamine hydrochloride and benzanilide.

Aniline and o-Toluidine.—Acetyl chloride gave with these substances in benzene solution acetanilide and a precipitate of *o*-toluidine hydrochloride. When acetic anhydride was added to a molecular mixture of aniline and the toluidine, the reaction product yielded, on investigation, acetanilide and *o*-toluidine, a result wholly in accordance with the action of the acetyl chloride.

When succinyl chloride was added to the aniline and *o*-toluidine suspended in water, the solid product formed consisted only of succinanilide; no trace of succintoluide was discovered, a result which corresponds to the action of the more simple acid chlorides.

These same two amines in benzene solution gave with benzoyl chloride mainly benzanilide and *o*-toluidine hydrochloride, while small amounts of *o*-benztoluide and aniline were also identified.

Aniline and p-Toluidine.—When acetyl chloride is added to a solution of aniline and *p*-toluidine in benzene, much heat is evolved and the solution contains acetanilide and the hydrochloride of *p*-toluidine.

Aniline and Pseudocumidine yield with acetyl chloride in benzene solution acetanilide and pseudocumidine hydrochloride.

Aniline and Phenylhydrazine. — The aniline and phenylhydrazine were suspended in water and benzoyl chloride added. The results were entirely in harmony with the preceding, benzanilide and the salt of phenylhydrazine being formed.

The second series of amines includes those that are more negative than aniline, giving as general products, more or less completely, aniline hydrochloride and the acyl derivative of the second amine.

Aniline and m-Nitroaniline were suspended in a large excess of water and benzoyl chloride added. The solid product proved to be the benzoyl derivative of *m*-nitroaniline, while the filtrate contained aniline hydrochloride and a little *m*-nitroaniline.

In benzene solution these amines gave mainly *m*-nitroacetanilide and the hydrochloride of aniline.

Aniline and p-Bromaniline.—In benzene solution the chief products with benzoyl chloride were *p*-brombenzanilide and

aniline hydrochloride. A little *p*-bromaniline and traces of benzanilide were also isolated.

Aniline and m-Brom-p-toluidine. — The amines suspended in water yielded with benzoyl chloride benzoic *m*-brom-*p*-toluide, and aniline hydrochloride.

Aniline and o-Anisidine.—Benzoyl chloride gave with the above as main products aniline hydrochloride and the benzoyl derivative of *o*-anisidine. A little benzanilide was also isolated.

Aniline and p-Phenetidine.—These give, either in water or benzene solution, mixtures of products, with the benzoyl-*p*-phenetidide predominating.

Aniline and m-Xylidine.—Like the preceding, aniline and *m*-xylidine tend to give with benzoyl chloride, when suspended in water, a mixture of products. The benzoyl-*m*-xylide, however, is in excess, while the filtrate contains the salts of aniline and some *m*-xylidine.

In comparison with aniline, a much greater proportion of the acyl *m*-xylide is obtained than with other methyl derivatives like *o*- and *p*-toluidines, and pseudocumidine, which are more positive to aniline.

Aniline and α-Naphthylamine.—These amines in benzene solution give with acetyl chloride chiefly α-acetnaphthalide and aniline hydrochloride, while in water solution with benzoyl chloride, there are obtained largely benzoic α-naphthalide and the aniline salt.

Aniline and β-Naphthylamine.—Acetyl chloride gave with these amines in benzene solution primarily acet-β-naphthalide and aniline hydrochloride, together with some β-naphthylamine.

o- and p-Toluidine.—In one experiment in ether solution with acetyl chloride *p*-acettoluide and *o*-toluidine were obtained, but in another case with benzoyl chloride a mixture of the two benztoluides resulted. The effect of the *o*-, *m*- and *p*-positions on the reaction will be investigated further.

Pseudocumidine and m-Xylidine.—These bodies when dissolved in benzene and treated with benzoyl chloride yielded the hydrochloride of pseudocumidine and benz-*m*-xylide, a result in accordance with their relative action toward aniline.

Aniline and Monomethylaniline.—Benzoyl chloride in water solution gave with these substances aniline hydrochloride, benzanilide, and an oily product which possibly contains some benzoyl-

monomethylaniline, but it has not as yet been obtained in a pure enough state for identification.

Aniline and Diphenylamine.—Molecular quantities of these amines yield in benzene solution benzanilide, aniline hydrochloride, diphenylamine and unchanged benzoyl chloride.

WASHBURN COLLEGE,
TOPEKA, KANSAS.

PIPERONAL AND HYDROGEN CHLORIDE: A TWO-COMPONENT THREE-PHASE SYSTEM.

BY F. J. MOORE.

Received June 7, 1906.

SINCE it appears from a recent paper by D. McIntosh,[1] that he is also studying the action of the halogen acids upon aldehydes, the following extremely incomplete observations are communicated at this time to avoid any possibility of collision.

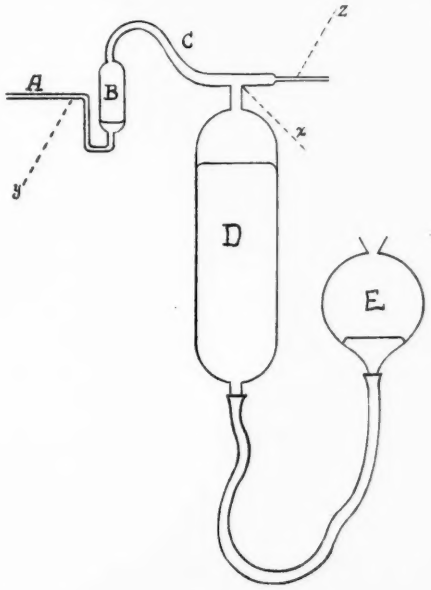
While investigating the action of some organic compounds upon piperonal, the accidental observation was made that this substance liquefies when brought into contact with dry hydrogen chloride. When the liquid thus formed was exposed to the air on a watch-glass, crystals appeared. A melting-point determination showed that these consisted of piperonal. The explanation of these phenomena obviously is, that piperonal adds hydrogen chloride as long as the pressure of the latter upon its surface is about one atmosphere, but the vapor pressure of the product is so great that when the partial pressure of the hydrogen chloride falls, all the gas is liberated. In order to bring out these relations more clearly, the apparatus was devised which is represented in the accompanying diagram.

B is a small bulb about 35 mm. high and 7 in diameter—outside measurement. D is a much larger cylinder about 135 mm. long and 40 in diameter. E is a leveling-bulb connected with D by thick-walled rubber tubing.

Somewhat less than a gram of piperonal is first introduced into B. The most convenient way to do this is to melt some piperonal, and draw it in through A by suction. Mercury is next poured into the bulb E, and the latter is raised until the mercury fills D and reaches the point x, just leaving the tube C open. Meanwhile the piperonal in B is kept melted by means of a beaker of

[1] This Journal, **28**, 588 (1906).

warm water placed under it, and now a stream of dry hydrogen chloride is passed through the bulb, entering through A. As soon as the current is started, the warm water under B may be removed, and the gas is passed through until the crystals which at first begin to form have completely liquefied. The tubes A and C are now sealed off at the points *y* and *z*. The mixture in B is now in equilibrium with the hydrogen chloride above it at the prevailing temperature, and the whole system stands under the pressure of one atmosphere.



If, now, the bulb E be lowered, gas is evolved from the liquid in B, which begins to boil. Crystals soon appear upon its surface, and, if the quantity of piperonal has been appropriately chosen with reference to the dimensions of the apparatus, the contents of B solidify to a mass of crystals. If the bulb E be again raised, the gas is absorbed, the crystals rapidly lose their outline, and, in less than a minute, those on the surface have completely liquefied. After standing at a pressure of about an atmosphere for a few

minutes, liquefaction is complete throughout the mass. These operations can, of course, be repeated indefinitely.

The conditions here seem analogous to those which obtain between calcium oxide, carbon dioxide and calcium carbonate at a temperature in the vicinity of 800°. As the action in the present case is so rapid, and can be so readily followed by the eye, it is suggested that the experiments just described might well find use in demonstrating to students this particular application of the "phase rule."

A rough measurement of the difference in level of the mercury in bulbs D and E, when both solid and liquid are present in B, shows that the dissociation pressure of the addition product is somewhere in the vicinity of 500 mm. This is but a rough approximation. An accurate measurement has not yet been attempted, as in the experiments hitherto made I could not be certain that the hydrogen chloride was free from air. Another form of apparatus has been designed to meet this difficulty, and when the work is resumed in the autumn, more accurate measurements will be made. The question whether the addition-product is a chemical compound or a solution will then be taken up, and the investigation extended to the action of hydrogen bromide and iodide as well as other compounds upon piperonal.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.
June 5, 1906.

BENZOYL-p-BROMPHENYLUREA: A BY-PRODUCT IN THE PREPARATION OF BENZBROMAMIDE.

BY F. J. MOORE AND A. M. CEDERHOLM.

Received June 7, 1906.

IN 1882, Hofmann,[1] while carrying on his celebrated investigation of the action of bromine and alkali upon amides, discovered acetbromamide. At the same time he made the observation that this substance reacts both with aniline and with phenol to form tribromaniline and tribromphenol respectively—acetamide being regenerated in accordance with the following equation.

$$C_6H_5.NH_2 + 3C_6H_5—CO.NHBr = C_6H_2(Br_3)NH_2 + 3C_6H_5CO.NH_2.$$

The chemical behavior of acetbromamide and analogous compounds has since been investigated by Seliwanow[2] and others,

[1] Ber. 15, 410 (1882).

[2] Ibid. 26, 424 (1893).

but the use of benzbromamide as a brominating agent seems not to have been adequately studied. An extended investigation of the subject is now being carried on in this laboratory. The results will be communicated later by one of us in connection with another collaborator. It is sufficient to say here that the products are not infrequently different from those obtained when bromine is employed.

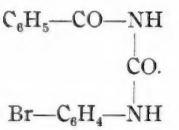
The occasion of the present investigation was an observation made while studying the action of benzbromamide upon phenol. If these substances are allowed to react in ethereal solution, the following apparent metathesis occurs, fully analogous to that observed by Hofmann.

$$C_6H_5OH + 3C_6H_5.CO.NHBr = C_6H_2(Br_3)OH + 3C_6H_5—CONH_2.$$

Mixed with the tribromphenol and the benzamide, however, there appeared another substance whose presence was, at first, not so easy to explain.

Properties of the By-product.—This substance is a white solid, insoluble in hot and cold water, and in cold dilute alkali, but soluble in cold concentrated sulphuric acid. It is insoluble in ether, but when boiled with large quantities of alcohol, benzene, or chloroform, it dissolves, and crystallizes from each of these solvents in extremely fine silky needles. It is somewhat more soluble in glacial acetic acid, and the crystals obtained from this solvent are a little more compact. When heated in a melting-point tube of the ordinary form, the substance decomposes in the vicinity of 227°, with the formation of a reddish brown sublimate. If the melting-point tube be sealed off at the top before the determination is made, the substance melts quite sharply at 230°, and decomposes 2° higher. These phenomena are very characteristic. The substance contains both nitrogen and bromine. It was at first supposed that it might be a product of the action of benzbromamide upon phenol, but it soon became evident that the new substance existed as an impurity in the benzbromamide employed. From the latter it is easy to separate on account of its insolubility in cold dilute sodium hydroxide. When the impure benzbromamide is washed with this reagent, a white residue is obtained. This contains the by-product together with some benzamide. The latter is readily removed by treatment with boiling water, which dissolves the benzamide.

Constitution.—The investigation had reached this point when our attention was called to a paper by Stieglitz and Earle[1] who prepared benzoyl-*p*-chlorphenylurea by the action of phenyl isocyanate upon benzchloramide, among other methods. The properties of the compound we were studying led us to suspect that it was the analogous bromine compound—benzoyl-*p*-bromphenylurea,



This view was supported by the following analysis:

	Calculated for $C_{14}H_{11}O_2N_2Br$. Molecular weight, 319.1.	Found. I.	Found. II.
C	52.65	52.73	.....
H	3.47	3.50	.....
O	10.02	.....	.....
N	8.80	9.21	.....
Br	25.06	25.08	24.98

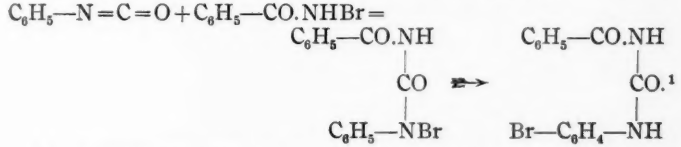
Syntheses.—As no description of a benzoylbromphenylurea was found in the literature, we were under the necessity of proving the constitution of the substance by synthetic methods. This was accomplished by means of reactions for the most part similar to those employed by Stieglitz and Earle in their study of the chlorine compound. One of these reactions, that of benzoyl chloride upon *p*-chlorphenylurea, was not available, as Pinnow[2] has studied the action of benzoyl chloride upon *p*-bromphenylurea, and found that it proceeds in a different sense, yielding benzonitrile and benzoyl-*p*-bromanilide. As the preparation of *p*-bromphenylurea itself offers some difficulties, it did not seem worth while to repeat this work on the chance of there being another product which Pinnow might have overlooked. This seemed all the more unnecessary as we were able to prepare the compound in four other ways: (1) by the action of phenyl isocyanate upon benzbromamide in benzene solution; (2) by the action of *p*-bromphenyl isocyanate upon benzbromamide in alkaline solution; (3) by the action of *p*-bromphenyl isocyanate upon benzamide when these substances are heated together; (4)

[1] Am. Ch. J. **30**, 412 (1903).

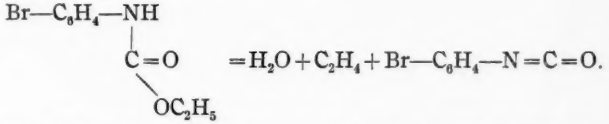
[2] Ber. **24**, 4172 (1891).

by the action of benzbromamide upon benzoylphenylurea in benzene solution. These syntheses leave no room for doubt that the compound has the constitution already indicated.

(1) *Preparation from Phenyl Isocyanate and Benzbromamide.*— For this experiment a specially prepared and purified sample of benzbromamide was employed which was completely soluble in cold dilute sodium hydroxide, and hence could have contained no appreciable quantity of the by-product under consideration. This material was used in all subsequent synthetic experiments where benzbromamide was required. Two grams of the pure benzbromamide were heated with 1.5 grams phenyl isocyanate and 5 cc. benzene on the water-bath. At 90° all went into solution, the mixture becoming deep red in color. Soon after, a bulky white precipitate appeared, and the supernatant liquid became nearly colorless. The precipitate was filtered off, washed with alcohol, dried and recrystallized from chloroform. The crystals thus obtained melted at 227° with decomposition, and when mixed with some of the by-product obtained from the impure benzbromamide, did not depress its melting-point. The yield was nearly quantitative. The reaction is as follows:



(2) *Preparation from p-Bromphenylurea and Benzbromamide.*— Some difficulty was experienced in preparing the *p*-bromphenyl isocyanate for use in this and the following synthesis. At first we followed the directions of Dennstedt[2] who treated *p*-bromphenyl urethane with phosphorus pentoxide in accordance with the following reaction:



Dennstedt states that the product can be distilled off from the

[1] The wandering of the halogen atom has been discussed by Stieglitz and Earle.

[2] Ber. 13, 228 (1880).

reaction mixture. In our experiments decomposition always sets in when distillation was attempted. The conditions were varied, but with no better result, and extensive decomposition was observed even when the heating was done in a bath, and the distillation conducted in vacuum. A little of the isocyanate sought could usually be identified in the distillate, but the quantity was utterly insufficient for use in further work. Attempts to distil were therefore abandoned, and the reaction mixture extracted with ligroin instead. In this way a yield of about 30 per cent. was obtained.

Four-tenths gram of the isocyanate was intimately mixed with one molecule of pure benzbromamide, and one molecule of sodium hydroxide added in the form of a 10 per cent. solution. The mixture was thoroughly shaken for twenty minutes, and then filtered. The precipitate was washed with water and then with cold alcohol. Finally it was recrystallized from hot alcohol. A melting-point comparison made as in previous cases, showed that this substance was identical with the by-product studied.

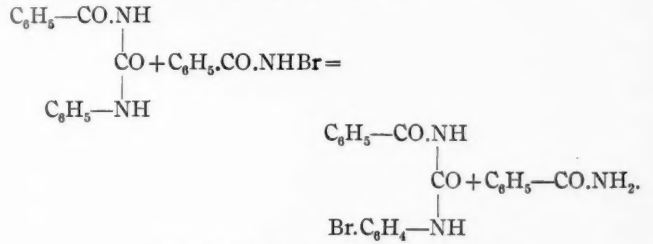
$$Br—C_6H_4—NCO + C_6H_5—CO.NHBr + NaOH = \begin{matrix} C_6H_5—CO.NH \\ | \\ CO \\ | \\ Br—C_6H_4—NH \end{matrix} + NaOBr.$$

(3) *Preparation from p-Bromphenyl Isocyanate and Benzamide.* —Two-tenths gram of the isocyanate (one molecule) was intimately mixed with benzamide (one molecule) and the mixture heated in an oil-bath at 175°—thermometer in bath. An odor suggestive of bitter almonds was noticed during the heating. The dark colored reaction product was treated with hot water to dissolve benzamide, and the residue washed first with alcohol, and then with chloroform, and finally crystallized from the latter solvent. The yield was small, but the product could be identified with the benzoyl-*p*-bromphenylurea produced by other methods.

$$Br—C_6H_4NCO + C_6H_5—CO—NH_2 = \begin{matrix} C_6H_5—CO.NH \\ | \\ CO. \\ | \\ Br—C_6H_4—NH \end{matrix}$$

(4) *Benzoylphenyl from Benzoylphenylurea and Benzbromamide.* —Benzoylphenylurea was prepared according to the method of

Kühn[1] by the action of phenyl isocyanate upon benzamide. The preparation presents no difficulties. 0.25 gram of the product was heated with 0.21 gram benzbromamide in benzene solution for about twenty minutes. On cooling, a bulky white precipitate appeared. This was washed with boiling water and finally recrystallized from chloroform. The usual melting-point tests showed it to be benzoyl-*p*-bromphenylurea which must have been formed by the following reaction:



HOW THE BY-PRODUCT IS FORMED.

Preparation of the Benzbromamide.—To three molecules of sodium hydroxide in 33 per cent. solution was added two atoms of bromine with constant shaking, the flask being surrounded by ice water, and pieces of ice also being added from time to time to the reaction mixture. As soon as all the bromine had been dissolved, one molecule of finely ground benzamide was added with the same precautions. Some of the benzamide usually remained undissolved. This was removed by rapid filtration with the aid of suction, broken ice being placed in the filter bottle to keep the filtrate cold. To this filtrate, dilute, ice-cold acetic acid was added as long as a precipitate formed. At this point a red color was observed and the solution smelled strongly of bromine. This must have come from the reaction of the acid upon some hypobromite or bromate present in the solution along with the excess of sodium bromide. The precipitate was then filtered off, freed as much as possible from the mother-liquor by suction, and dried on porous plates. It was usually left spread out on these over night, and then crystallized from boiling benzene. Two crystallizations were usually necessary to secure a colorless product. The crystals thus obtained were flaky in structure, and the forms were not well marked.

[1] Ber. 17, 2880 (1884).

It will be observed that the method just described closely follows the directions of Hoogewerff and Van Dorp[1] also recommended by Hantzsch.[2] It differs in the use of sodium instead of potassium hydroxide and also in the use of an alkali solution which was more concentrated at the beginning of the reaction. As ice was added freely while the reaction progressed, the solution was probably as dilute at the end of the reaction as in the experiments of Hoogewerff and Van Dorp.

In our first experiments, about 50 grams of benzamide were used for each preparation. Later, when it became necessary to prepare especially pure material, only 10 grams were used, and about the same routine followed, except that additional pains were taken to perform all operations as slowly and at as low a temperature as possible. The substance prepared in this way crystallized in lustrous plates and was entirely soluble in cold dilute sodium hydroxide.

The impure product first described showed a tendency to grow reddish in color on standing, and emitted an odor resembling that of bromine. This led us to think that the formation of the brominated urea might be traced to a spontaneous decomposition of the benzbromamide, either while drying in contact with the dilute acetic acid or in the benzene solution during the process of crystallization, or, finally, by standing in the bottle. Various experiments were made to test these points, the details of which need not be given here. The crystalline impure benzbromamide was allowed to stand at various temperatures, both dry and in the presence of dilute acetic acid; it was also boiled with a return condenser for varying lengths of time both in benzene and in toluene solution. In none of these cases was it apparent that the amount of benzoyl-*p*-bromphenylurea in the product had perceptibly increased. The cause of its formation had, therefore, to be looked for at some earlier stage.

CONCLUSION.

We finally concluded that the key to the solution of this problem was to be found in an observation of Van Dam and Aberson.[3] These investigators found that a dilute solution of the potassium salt of benzbromamide decomposes with the formation of benzoyl-

[1] Rec. trav. chim. 8, 188 (1889).
[2] Ann. 296, 86 (1897).
[3] Rec. trav. chim. 19, 318 (1900).

phenylurea, and further that the reaction proceeds more rapidly in this sense, the more nearly neutral the solution. This behavior can be represented by the following equations, assuming the presence of some phenyl isocyanate at this point, (this would be in harmony with the views of most students of Hofmann's reaction):

(1) $C_6H_5—CONNaBr = NaBr + C_6H_5NCO.$

(2) $C_6H_5NCO + C_6H_5CONNaBr + H_2O = NaOBr + \begin{matrix} C_6H_5.CO.NH \\ | \\ CO, \\ | \\ C_6H_5—NH \end{matrix}$

or if with E. Mohr,[1] sodium phenylcarbamate is assumed as an intermediate product,

(1) $C_6H_5.CO.NNaBr + NaOH = NaBr + C_6H_5—NH.COONa.$

(2) $C_6H_5CO.NNaBr + C_6H_5NH.COONa + H_2O =$

$$NaOH + NaOBr + \begin{matrix} C_6H_5—CO.NH \\ | \\ CO. \\ | \\ C_6H_5—NH \end{matrix}$$

In the preparation of benzbromamide, when the acetic acid is added, the neutral solution favorable for these reactions is produced, and the precipitate consists of a mixture of benzbromamide and benzoylphenylurea. When this mixture is crystallized from benzene, the latter is brominated by the former in accordance with the reactions described in the fourth synthesis mentioned above. In fact this synthesis was originally carried out to test this very point.

Another possibility has to be considered. It has been already noted that when the acetic acid is added, some bromine seems to be liberated. This might effect the bromination. We are inclined to reject this hypothesis, partly because the last synthesis just alluded to has shown that the benzbromamide can accomplish this result, partly because Van Dam and Aberson and other investigators have only observed the non-brominated product, and partly because where the brominated urea has been met with, it has been accompanied by benzamide. The presence of the latter can be most easily accounted for on the assumption that

[1] J. pr. Chem. [2] 73, 177 (1906).

benzbromamide is the brominating agent. Furthermore, it is not easy to see why a substance as insoluble as benzoylphenylurea should be much affected by dilute bromine water.

The improvement in the quality of benzbromamide when only small quantities were prepared, is doubtless to be explained by the fact that, under these circumstances, it is easier to maintain a low temperature throughout, less of the benzbromamide being decomposed to form isocyanate or carbamate.

SUMMARY.

When benzbromamide is prepared by the method of Hoogewerff and Van Dorp, it is liable to contain benzoyl-*p*-bromphenylurea. The amount of this substance may sometimes exceed 10 per cent.

Benzoyl-*p*-bromphenylurea is a bulky, colorless, crystalline solid. It melts in a closed tube at 230° and decomposes at 232°. It is soluble with difficulty in most of the ordinary organic solvents.

The constitution assigned to this compound is most conclusively proved by its synthesis from *p*-bromphenyl isocyanate and benzamide, but it is also consistent with its preparation by three other syntheses, with the analysis, and with its whole behavior.

The formation of the benzoyl-*p*-bromphenylurea in the preparation of benzbromamide is to be accounted for as the result of the bromination of the benzoylphenylurea first formed. This bromination is probably effected by the benzbromamide itself.

The authors perform a pleasant duty in acknowledging their indebtedness to Dr. Richard B. Earle, instructor in organic chemistry at the institute, for many helpful suggestions.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.
June 5, 1906.

NOTES ON SOME OF THE CONIFER OILS.

BY R. E. HANSON AND E. N. BABCOCK.
Received June 20, 1906.

AN apparent want of conformity in the present literature on some of the conifer oils has led us to investigate several of them, and we hereby embody the results of our work.

Our investigation has been confined to the following oils:

(A) Black spruce (*Picea Mariana*) leaves.
Hemlock (*Tsuga Canadensis*) leaves.
(B) American larch (*Larix Americana*) leaves.
White spruce (*Picea Canadensis*) leaves.
White spruce (*Picea Canadensis*) cones.
Red spruce (*Picea rubens*) leaves.
Red spruce (*Picea rubens*) cones.
Pitch pine (*Pinus rigida*) leaves.
Red pine (*Pinus resinosa*).
Juniper (*Juniperus communis*) leaves.

All of the oils in division marked B are, to the best of our knowledge, distilled and herein described for the first time.

Throughout the work we have carefully identified all materials from which the oils have been distilled and have personally superintended the distillation to insure the purity of the oils.

(1) *Oil of Black Spruce* contains 48.85 per cent. bornyl acetate (Kremers), sp. gr. 0.922 at 20° (Gildmeister and Hoffmann). An oil distilled by us was obtained in a yield of 0.57 per cent. and had a sp. gr. of 0.9274 at 19°. Change in the specific gravity of its fresh oil for 1°, 0.0010; for oil which has stood for some time 0.0014.

(2) *Oil of Hemlock* contains 51.5–52 per cent. of bornyl acetate —sp. gr. 0.9288 at 20° (Hunkel). According to Gildmeister and Hoffmann, it contains 36 per cent. bornyl acetate, sp. gr.0.907–0.913. An oil distilled by us from leaves and twigs of a large tree was obtained in a yield of 0.4 per cent., sp. gr. 0.9238 at 15°. A second distillation from the leaves and twigs of a small tree gave a yield of 0.46 per cent., sp. gr. 0.9273 at 15°. Change in its specific gravity of the fresh oil for 1°, 0.0010.

(3) *Oil Picea Canadensis* (Cat Spruce) has apparently not been investigated, although we have reason to believe it is often confused with black spruce in the distillation of the latter. We obtained this oil in a yield of 0.103 per cent., sp. gr. 0.9216 at 15°. Change in the specific gravity for 1°, 0.0012. It contains 25.7 per cent. of ester, calculated as bornyl acetate, which is a low ester content in comparison with the other spruce oils. The odor of this oil is distinctly different from that of black spruce and hemlock oils, suggesting limonene or dipentene. We are at

present engaged upon the identification of the terpenes present in this oil.

(4) *Oil Picea Rubens* (Red Spruce).—This oil is remarkable for its high specific gravity and high percentage of ester. The distillation gave a yield of 0.204 per cent., sp. gr. 0.9539 at 16°. Change in the specific gravity for 1°, 0.0014. This oil contains 66.2 per cent. of bornyl acetate and 7.76 per cent. of free borneol. On saponification, large quantities of crystals having a distinct odor of borneol separated out. After recrystallizing several times from petroleum ether the borneol appeared as white, shining, hexagonal plates melting, but not sharply, in the neighborhood of 200°. Lack of sufficient quantity of oil prevented us from obtaining crystals with the melting-point of pure borneol, 206°, or from forming derivatives and thus making a positive identification.

The oil itself had a very agreeable odor, strongly suggestive of borneol acetate.

(5) *Oil Larix Americana.*—This oil, distilled from the leaves and twigs was obtained in a yield of 0.149 per cent., sp. gr. 0.8816 at 15°, ester content 15.1 per cent., calculated as bornyl acetate.

Fractional distillation gave the following results:

155°–170°	= 20	per cent.
170°–180°	= 38.4	" "
180°–190°	= 11.2	" "
190°–200°	= 9.2	" "
200°–240°	= 14.8	" "
Residue	= 6.4	" "
Total	= 100	" "

The fraction 170–180° was redistilled when 62 per cent. boiled below 171°; 20.5 per cent. boiled at 171–181°. The remainder was the residue, boiling above 181°.

The fractions distilling *below* 171° were combined. The specific gravity of these combined fractions was 0.8578 at 15°. Two more redistillations of the fractions below 171° yielded a fraction boiling at 155–162°. From this last fraction we were enabled to obtain a nitrosochloride which melted sharply at 108°. This is the melting-point of pure pinene nitrosochloride.[1] Owing to paucity of material, we did not attempt to form the nitrol-

[1] Van Romburgh: See Schimmel's Report, April, 1901.

benzylamine compound, which would have established still more firmly the presence of pinene.

According to our investigations, 15.1 per cent. of this oil is ester (calculated as bornyl acetate) and the remainder is largely pinene.

(6) *Picea Rubens* (*Cones*).—This oil was obtained in a yield of 0.38 per cent., sp. gr. 0.8600 at 15°, with a golden yellow color and a fir-balsam-like odor.

(7) *Oil of Picea Canadensis* (*Cones*).—This oil was obtained in a yield of 0.25 per cent., sp. gr. 0.899 at 15°. It was of a yellow color and a pronounced limonene-like odor. These constants were taken some time after the oil had been distilled, and the high specific gravity may be due to a subsequent thickening.

(8) *Oil Pinus Rigida.*—The yield of this oil was extremely small. From 12 kg. of leaves and twigs we obtained only 0.2 cc. Oil was yellow in color and had an extremely pungent odor.

(9) *Oil Pinus Resinosa.*—The yield of this oil was also very small, about 0.001 per cent. The color of the oil was a brownish red. Its odor was very pungent and disagreeable.

(10) *Oil Juniperus Communis.*—Leaves and twigs, devoid of berries, were used in the distillation of this oil. The oil was obtained in a yield of 0.18 per cent. in one distillation, while a second distillation of material from other ground gave nearly the same yield, 0.15 per cent. These distillations were carried on in the spring about the first of May. Specific gravity of the oil was 0.8531 at 20°. Oil was of a light yellow color and characteristic juniper odor.

(11) *Oil Juniperus Virginiana* (*Leaves*).—An oil distilled by us had a slightly higher density than is generally given. Sp. gr. 0.900 at 16°.

Owing to lack of sufficient quantities of the oils we have been unable to carry these investigations further as yet. Arrangements are being made, however, for the distillation of larger quantities of several of them as well as other new oils of the same species. We hope to be able to present more complete results in the near future.

READING, MASS.

THE DETECTION OF METHYL ALCOHOL.

By Heywood Scudder and Robert B. Riggs.

Received June 23, 1906.

Leach and Lythgoe[1] recommend as a confirmatory test for the detection of methyl alcohol, oxidation of the solution by a hot copper spiral and testing for formaldehyde by heating with milk and hydrochloric acid containing ferric chloride.

We have tried this test on 10 per cent. aqueous solutions of ethyl alcohol, acetic acid and acetone, and in each case there developed a violet color indistinguishable from that given by pure methyl alcohol. After oxidation the solutions were filtered before adding the milk and acid. The color obtained depends somewhat on the conditions of the test. Leach directs the use of a few drops of the oxidized solution.

In the case of acetone, if the whole of the oxidized solution was used, a distinct violet color appeared momentarily during the heating, changing to a brownish yellow. If only a few drops of the oxidized solution were used the violet color was deep and persistent. But on adding to this the rest of the oxidized solution (which contained a good deal of unaltered acetone) and heating, the violet color disappeared, changing to brownish yellow. In this case the excess of the acetone gave a color that obliterated the color due to formaldehyde.

In the case of ethyl alcohol there is a difference in the depth of the violet color between tests made with a few drops and with the whole of the oxidized solution, but the violet always persists.

Acetic acid showed no difference in color whether a few drops or the whole solution was used.

Oxalic acid gave a brown with a faint violet tinge, when a few drops of the oxidized solution were tested, but excess of the oxidized solution destroyed this violet, leaving only the brown. The violet tinge was sufficiently marked to be noticeable to one unaccustomed to the test.

A blank test of the milk used, showed no trace of a violet tinge under any variations of heating.

The cause of the failure of this test is its delicacy in detecting formaldehyde. The formation of small amounts of formaldehyde in the oxidation of many organic compounds, especially

[1] This Journal, 27, 965 (1905).

when the oxidant is heated copper or platinum, is well-known,[1] and warnings have been given of the caution necessary in applying any test for methyl alcohol that depends on a very delicate test for formaldehyde.

In the case of the compounds tested, the violet color came from formaldehyde. If a sufficient amount of some other compound reacting with milk and acid was present (as in the case of acetone and oxalic acid) the violet color became changed or obliterated, otherwise it persisted.

In its present condition this test can not be depended on as a general one for the detection of methyl alcohol in mixtures.

The Sanglé-Ferrière Cumiasse Test[2] we have modified so that it can be performed more simply. This modification shows 2 to 3 per cent. of methyl alcohol in ethyl. To 10 cc. of the aqueous solution to be tested are added 0.5 cc. of concentrated sulphuric acid and 5.0 cc. of a saturated solution of potassium permanganate. The temperature should be kept at 20°–25°. At the end of two minutes enough sulphurous acid is added to give a colorless solution (an excess is not harmful). The solution is boiled till it does not smell of sulphur dioxide nor of acetaldehyde, then the resorcinol test for formaldehyde is applied. If no flocks appear but a pink ring is present, they can often be developed by standing for one to two hours, then heating the upper layer just to boiling. The ring first formed is usually sufficiently characteristic to show methyl alcohol and in case of doubt a blank test with ethyl alcohol can be made, but the flocks give positive evidence and no blank is required.

The use of sulphurous acid to reduce any excess of the permanganate and to dissolve the hydroxide avoids the troublesome precipitation by tannic acid and sodium carbonate with subsequent filtration.

Variations in the temperature below 18° are harmful from the reduced speed of the reaction, above 30°, from loss of formaldehyde. Great excess of acid is harmful. Less acetaldehyde seems to be formed from ethyl alcohol in this oxidation than in the oxidation with a hot copper spiral.

Formation of Flocks in the Resorcinol Test for Formaldehyde.—

[1] Mulliken, Brown, French: Am. Ch. J. 25, 115 (1901); Scudder: This Journal, 27, 894 (1905).

[2] Ann. chim. anal. appl. 8, 82 (1903).

If to the solution to be tested are added an equal volume of concentrated hydrochloric acid and two drops of a 0.5 per cent. solution of resorcinol and the whole is boiled one or two minutes, characteristic flocks will appear, if sufficient formaldehyde is present.

The advantage of using hydrochloric acid instead of sulphuric acid is that no darkening of color from overheating or charring is possible. The disadvantage is that the delicacy of the test is lessened. It is not possible to get flocks in mixtures of methyl and ethyl alcohols when less than 5 per cent. methyl alcohol is present. The boiling, of course, prevents any formation of a contact ring. But when sulphuric acid is used, the color of the flocks is often destroyed by too rapid shaking, with consequent overheating, especially when only a small amount of formaldehyde is present.

TRINITY COLLEGE, HARTFORD.

A METHOD FOR THE DETERMINATION OF LEAD NUMBER IN MAPLE SYRUP AND MAPLE SUGAR.

BY A. L. WINTON AND J. LEHN KREIDER.

Received July 5, 1906.

THE copious precipitate formed in maple products by basic lead acetate furnishes a means not only of clearing the solution for polarization but also of detecting the admixture of refined cane-sugar. Jones[1] and also Hortvet,[2] working independently of each other, have devised methods for measuring the bulk of this precipitate after separation with the aid of a centrifuge. The method devised by Jones was especially designed to test the products delivered by farmers to wholesalers, while Hortvet's method was devised with reference to the official inspection of the commercial products. Both serve well the purpose for which they were intended; they are easily carried out and give comparative results of great value. These results, however, can hardly be accepted as fixed constants, since the precipitate varies not only in composition but its volume is also dependent on the speed of the centrifuge and other details of manipulation.

Although volumetric methods of a similar nature are successfully employed for the determination of the gravimetric per-

[1] Vt. Agr. Expt. Sta. Rep. 17, 454 (1904).

[2] This Journal, 26, 1532 (1904).

centages of fat (*e. g.*, Babcock method) and essential oil (*e. g.*, Mitchell's method for determining the oil in lemon extract), it is impracticable to convert the volume of a solid precipitate into percentages even when the precipitate is of definite composition and the task is obviously impossible when it is a variable mixture.

It also appears to us impracticable to weigh this precipitate, owing to difficulties in filtering, washing and drying.

The plan which seems to best serve the purpose is not to determine the total percentage of the precipitate but the amount of lead contained in it. This lead could be determined in the precipitate itself but this would involve careful washing and separation from the organic matter, both of which are laborious operations.[1] We have employed an indirect method, using a definite volume of standard lead subacetate and determining the lead remaining in the solution after precipitation. In order to still further reduce the labor of the operation the solution of the material after precipitation is made up to a definite volume, filtered through a dry paper, and the lead determined as sulphate in an aliquot portion of the filtrate.

The method adopted by us is in detail as follows:

Description of the Method.[2]—Weigh 25 grams of the material (or 26.048 grams if it is desired to determine sugars polariscopically in the same portion) into a 100 cc. flask. Add 25 cc. of standard lead subacetate solution, fill to the mark, shake, allow to stand at least one hour, and filter. From the clear filtrate pipette off 10 cc., dilute to 50 cc., add a moderate excess of sulphuric acid and 100 cc. of 95 per cent. alcohol. Let stand over night, filter on a Gooch crucible, wash with 95 per cent. alcohol, dry at a moderate heat, ignite at low redness for three minutes, taking care to avoid the reducing cone of the flame, and weigh. Calculate the amount of lead in the precipitate (factor 0.6829), subtract this from the amount in 2.5 cc. of the standard solution, and divide the remainder by 2.5 thus obtaining the "*Lead Number.*"

The standard lead subacetate is prepared as follows:[3] Boil for half an hour 430 grams of normal lead acetate and 130 grams of

[1] Since this paper was read at the Ithaca meeting of the Society (June 28, 1906) Prof. Albert P. Sy has published a paper describing a method of determining the lead directly in the precipitate (J. Franklin Inst. July, 1906, p. 71).

[2] Devised by A. L. W.

[3] U. S. Dept. Agr., Div. Chem. Bull. 65, p. 84.

litharge with 1000 cc. water. Cool the mixture, allow to settle, and dilute the supernatant liquid to 1.25 specific gravity. To a measured amount of this solution add four volumes of water and filter if not perfectly clear.

The standard of the solution is determined in 25 cc. by the lead sulphate method as above described. On standing it deposits a slight precipitate, but our tests show that the strength is not appreciably affected in a month or six weeks.

Given sufficient Gooch crucibles about 24 determinations of the lead number can be made in eight hours distributed through two days.

Test of Different Standard Solutions, Time Required for Precipitation.—As basic lead acetate solution varies somewhat in composition dependent on impurities in the chemicals used and irregularities in the process of preparation, it is important to ascertain whether these variations affect the precipitating power. It is equally important to determine the time required for complete precipitation. To decide these points comparative analyses were made on three samples of pure and three of adulterated maple syrup, using three solutions prepared from different lots of chemicals and allowing to stand after the precipitation one and eighteen hours. Solutions A and B were prepared from different lots of commercial lead acetate and litharge, solution C from the chemically pure materials.

The results are given in Table I.

TABLE I.—COMPARISON OF RESULTS ON LEAD NUMBER IN PURE AND ADULTERATED MAPLE SYRUPS, USING DIFFERENT STANDARD SOLUTIONS OF LEAD SUBACETATE AND STANDING ONE AND EIGHTEEN HOURS AFTER PRECIPITATION.

	Pure.						Adulterated.					
	No. 15988.		No. 15989.		No. 16037.		No. 15967.		No. 15970.		No. 15993.	
	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.	1 hr.	18 hrs.
Solution A	1.88	2.04	1.52	1.62	1.63	1.84	0.00	0.00	0.16	0.13	0.46	0.44
" B	2.03	2.12	1.60	1.64	1.71	1.93	0.02	0.02	0.13	0.18	0.31	.....
" C	2.14	2.05	1.70	1.82	1.94	1.93	0.00	0.04	0.23	0.31	0.34	.....

From these results it appears that no fear need be apprehended as to variations in the precipitating power of the standard solution, also that standing one hour gives virtually the same results as standing eighteen hours.

It should here be stated that in the case of all the pure samples,

which we have examined, the solution filtered from the lead precipitate after standing one hour remained clear on further standing. The same is also true of all the adulterated samples but one. The latter, No. 16036 Table III, gave a lead number of 0.13 on standing one hour and of 0.42 on standing eighteen hours. Since one hour was found sufficient for all pure samples it is reasonable to assume that the extra amount obtained on long standing from this adulterated sample is due to some foreign constituent and may be justly disregarded.

Results on Authenticated Samples.—The following results, obtained on samples of known purity kindly supplied by Mr. C.

TABLE II.—RESULTS ON LEAD NUMBER AND TOTAL SOLIDS IN AUTHENTICATED SAMPLES OF MAPLE SYRUP AND MAPLE SUGAR.

No.		Total solids.	Lead number.
1	Maple syrup, excellent quality, composite sample.....	64.16	1.54 1.54
2	" " " " " "	64.07	1.39 1.38
3	" " " " " " (Ohio)	68.49	1.21 1.19
4	" " " " (made in 1893).....	64.53	1.49 1.47
5	" " good quality, composite sample.....	68.28	1.66 1.66
6	" " medium quality, " "	66.21	1.57 1.57
7	" " " " " "	64.86	1.40 1.40
8	" " poor quality.....	65.59	1.77 1.77
9	Maple sugar (American), good quality.....	99.24	2.07 2.10
10	" " " " "	99.20	2.37 2.38
11	" " " medium quality.....	98.99	2.30 2.29
12	" " " " "	98.43	2.47 2.48
13	" " " composite sample.....	99.28	2.18 2.17
14	" " (Canadian), good quality.....	94.99	2.35 2.36
15	" " " " "	94.63	1.83 1.84

H. Jones, chemist of the Vermont Station, give a general idea of the variation in the lead number in the normal product although these results should be supplemented later by others on samples from other localities before the range in the lead number can be finally decided.

Results on Samples Found on the Market.—We have recently made analyses of 38 brands of maple syrups found on sale in Connecticut which show that only three were the genuine products, the remainder being mixtures consisting largely of refined cane-sugar. The determinations made include not only lead number but also, for comparison, total solids, cane-sugar (by Clerget's formula), Hortvet number (volume of the lead precipitate), and total ash. The lead number in the samples classed as pure ranged from 1.61 to 2.03, while in the adulterated samples it ranged from 0.02 to 0.92. In Table III are given such of these analyses as serve to show the range in composition of the samples.

It is a remarkable fact that every result in this table, except those for total solids and sucrose, furnishes decided evidence of purity or adulteration. Even the percentages of total solids and sucrose are useful, since the difference between the two is usually greater in the case of the pure syrups.

For a consideration of other methods of value in detecting adulteration the reader is referred to the exhaustive papers of Hortvet[1] and Jones.[2]

It has been suggested that the lead number of adulterated maple products can be so increased by the addition of various substances as to equal that of the genuine products. That this is true can not be denied, but it is also true that the results for ash and other constituents of these products as well as many of the constants of other food products can be rendered valueless as a means of detecting adulteration by skilful manipulation. The task, however, becomes more difficult with the introduction of new constants, especially when these are based on different principles.

The determination of ash and its characters and of lead number will usually suffice for the detection of the adulterants now in common use.

[1] Loc. cit.

[2] Loc. cit.; Vt. Agr. Expt. Sta. Rep. 18, 315 (1905).

TABLE III.—ANALYSES OF MAPLE SYRUP FOUND ON THE MARKET.

Serial number.		Total solids. Per cent.	Sucrose by Clerget's formula. Per cent.	Hortvet number.[1]	Lead number.	Total ash. Per cent.
15988	Pure.....	66.98	62.4	1.00	2.03	0.75
15989	Pure.....	67.29	61.6	0.69	1.61	0.60
16037	Pure.....	66.40	59.5	1.24	1.89	0.54
15929	Adulterated[2].	66.40	65.4	0.15	0.66	0.14
15932	Adulterated..	66.90	65.4	0.15	0.48	0.16
15945	Adulterated..	65.81	.....	0.22	0.87	0.23
15948	Adulterated..	67.61	67.8	0.07	0.52	0.04
15961	Adulterated..	63.18	.....	0.07	0.10	0.02
15967	Adulterated..	68.62	67.6	0.07	0.02	0.04
15970	Adulterated..	66.58	65.2	0.11	0.19	0.19
15971	Adulterated..	69.49	68.4	0.11	0.43	0.07
15982	Adulterated..	64.53	61.9	0.15	0.17	0.17
16005	Adulterated..	65.57	.....	0.15	0.12	0.04
16006	Adulterated..	66.13	65.2	0.11	0.66	0.08
16035	Adulterated..	65.33	60.0	0.12	0.92	0.14

AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN, CONN.

ON THE DETERMINATION OF CARBON DISULPHIDE AND TOTAL SULPHUR IN COMMERCIAL BENZENE.

BY EDWARD S. JOHNSON.

Received July 7, 1906

CRUDE, unwashed benzene, or the so-called "benzol light oil," contains as certainly identified sulphur compounds, hydrogen sulphide, carbon disulphide, thiophene and its homologues. There are doubtless others among the unsaturated compounds which become eliminated in the first stage of benzene purification, the washing with concentrated sulphuric acid. There is left after this treatment in the lower-boiling fractions derived from the washed benzene, as a main impurity carrying sulphur, carbon disulphide. Thiophene, as well-known, represents the chief of other sulphur bodies present.

I. THE DETERMINATION OF CARBON DISULPHIDE.

The principle underlying the method seemingly most widely practiced is that of the transformation of carbon disulphide by means of alcoholic potash into potassium xanthate, utilizing this

[1] Cubic centimeters of lead precipitate from 5 grams of the material.

[2] The adulterated samples were mixtures of maple syrup and refined cane-sugar. Some were labeled as compounds and therefore were not legally adulterated.

substance as a medium of separation for the sulphide. For the determination of the sulphide the xanthate has variously been weighed as such, converted into cuprous xanthate, and again titrated with cupric sulphate solution. Nickels[1] seems first to have applied the xanthate reaction to a separation of carbon disulphide from benzene. The volumetric method referred to originated with Macagno[2] with a view, however, of applying the process to the assaying of carbon disulphide preparations.

The method of Nickels[3] to determine the sulphur finally by weighing the potassium xanthate or cuprous xanthate derived from it *as such* is attended by several inaccuracies. When operating with the potassium salt it must be separated by filtration and washed with ether. The mother-liquors are merely drawn or drained off and leave a precipitate contaminated by adhering alkali not removed by the ether. It is constantly undergoing decomposition on exposure to air. The cuprous salt is more stable but cannot be brought to constant weight without decomposition even by moderate warming after water-washing. By ether treatment of the precipitate freed from the mother-liquors, a more successful drying might result. In view of the somewhat unstable character of the compound, however, the determination as copper oxide, after ignition of the precipitate, promised more satisfactory results. Much uncertainty exists apparently as to the exact composition of the so-called cuprous xanthate. If constituted as represented by the formula $(CS.OC_2H_5S)_2Cu_2$, the ratio of copper oxide produced to carbon disulphide entering into the formation of the xanthate should be 1.0:0.9563. In establishing the basis of his volumetric method, Macagno made some determinations of the ratio and found 1.0:1.931 not much varying from *twice* the theoretical. Others have obtained similar results indicating approximately the relationship $2CS_2:CuO$. As evidently cuprous xanthate is not the compound under consideration, judging from the ratios thus discovered, and recalling the instability of the body resulting from the action of cupric sulphate on potassium xanthate, a reopening of the question as to the ratio of the copper compound obtained on ignition of the xanthate produced by a known weight of carbon dioxide seemed

[1] Chem. News, 43, 148.
[2] Ibid. 43, 138.
[3] Attributed to him by Allen: Comm. Organ. Anal.

justified. An investigation appeared the more desirable because of a strong probability of a variation in composition with changing conditions of formation. Experiments were, therefore, made, having in mind a process for the separation and determination of carbon disulphide contained in benzene by means of the xanthates, the method being adapted to convenient manipulation and conditions easily realized and thus maintained constant. The ratio of copper oxide, yielded by the yellow xanthate upon ignition, to the carbon disulphide from which it was derived under the given circumstances was made the subject of the experiments, an account of which follows:

1. *Determination of the Ratio of the Copper Ignition-Residue to Carbon Disulphide.*

That the ratio might be an expression of the many experimental factors in a determination of carbon disulphide in benzene, known weights of a perfectly pure sulphide were dissolved in a specially prepared benzene, the sulphide transformed into potassium xanthate, which was separated and determined, as to be described.

The Separation of the Carbon Disulphide as Xanthate.—As intimated above, the matter-of-course precaution was taken to apply a preparation of carbon disulphide of high purity, and the usual manipulations in the weighing and transfer of so volatile a substance without loss were employed. The weighed portions of the sulphide were added to about 75 cc. of pure benzene contained in a glass-stoppered flask of 250 cc. capacity. Besides the benzene the flask already contained for each 0.1 gram of carbon disulphide about 1 cc. of a saturated alcoholic solution of potassium hydroxide. The sulphide was then liberated from the weighing vessel and the mixture agitated fifteen to twenty minutes. The potassium xanthate formed was dissolved by addition of water, and the aqueous xanthate solution and benzene transferred to a separating funnel. The solution was drawn off and the benzene well washed. The extraction was repeated with about three-quarters of the original amount of potassium hydroxide solution, and a third time should a separation of xanthate crystals occur in a second extraction. The extracts and washings were diluted to 500 cc. and aliquot parts applied for precipitation.

The Precipitation as Cuprous Xanthate and Determination as

Copper Oxide.—The alkaline xanthate solution was acidified with acetic acid, used well diluted and in very slight excess. Immediately the cold solution was treated with copper sulphate solution (1 : 5) in distinct but not great excess. During standing for one to one and one-half hours after the precipitation, the precipitate was repeatedly stirred. It has most agreeable qualities for quantitative manipulations. Filtration and water-washing are expeditious and perfect. The filtrate passed the filter clear as did the washings, as just implied, but upon standing for some hours, for instance over night, slight further precipitation invariably took place. In the experiments under discussion, this precipitate was collected and added to the main portion. In the usual technical analysis the amount of xanthate here concerned is so small as to become negligible. This second precipitation is presumably caused by dissolving of the compound in the washings in which it is more soluble than in the liquors in which it forms.

At once after the washing the precipitate was removed to a porcelain crucible, dried and ignited. A constant weight was easily obtained. The product of the ignition, in the main copper oxide, may also contain, where large precipitates are involved, some cuprous sulphide, a consideration which evidently in nowise disturbs the ratio sought.

2. *The Data Obtained.*

In the table below are found the results of a number of determinations of the CS_2-CuO ratio. No pretense is here made to an exhaustive investigation of the subject. Those points only which plainly require consideration for the purpose of establishing a method of sufficient accuracy for technical application were given attention. The variation in the ratios developing under circumstances defined in the table indicate need of still more detailed limitation of conditions. The relation of the xanthate to the quantity of alcoholic potash by which it is formed, the acidity and dilution of the solution upon precipitation of the copper salt and the excess of copper sulphate are all factors which, when exactly determined and considered, would eliminate in all probability, variations in the ratios appearing under identity of those conditions thus far investigated.

THE RATIO OF COPPER OXIDE TO CARBON DISULPHIDE UNDER VARYING CONDITIONS OF EXPERIMENT.

No.	CS_2.	Excess $CuSO_4$.	Age of xanthate solution.	Time for precipitation.	CuO.	CuO : CS_2. CuO = 1.0.
3	0.06038	Slight	Fresh	0 hrs.	0.0349	1.730
4	0.06038	Moder.	"	16 "	0.0379	1.593
7	0.06038	"	2-3 das.	1½ "	0.0354	1.706
1	0.08534	Large	Fresh	¾ "	0.0488	1.749
2	0.08534	Moder.	"	¾ "	0.0474	1.800
5	0.08534	Slight	3 das.	1 "	0.0494	1.728
8	0.13710	Moder.	Fresh	¼ Stir.	0.0747	1.825
9	0.13710		2 das.	20 hrs.	0.0805	1.703
10	0.13710	Moder.	3 "	1½ "	0.0770	1.780

In comparison with the results of former work, a much *lower ratio* is seen to exist under the circumstances detailed. The average is 90 per cent. of the Macagno ratio.

Among the factors taken into account in the present series of experiments, those of the size of the precipitate (quantity of carbon disulphide present) and time of standing before filtration appear as of most significance. The results from the use of 0.06 gram of carbon disulphide are about 5 per cent. lower than when 0.14 gram was applied. The influence of time on the precipitation is shown by 3 and 4, and again by 9 and 10; the former instances, for the longer period, show an 8 per cent. lower ratio; the latter, one by 4 per cent. lower. As representing the results to be obtained by the method described, No. 7 for 0.06 CS_2, Nos. 2 and 5 for 0.085 CS_2 and No. 10 for 0.14 CS_2 have been selected as working factors and the average as a general working factor. An extreme difference of about 4.0 per cent. exists. With a benzene containing 2 per cent. carbon disulphide, a variation of less than 0.10 per cent. would be involved by the use of the lowest and the highest factor. The average of 1.750 was adopted for general practice.

WORKING FACTOR IN RELATION TO CARBON DISULPHIDE CONCERNED IN ITS PRODUCTION AND THE AVERAGE FACTOR.

CS_2.	Working factor.	Average factor.
0.06038	1.706	1.676
0.08534	1.764	1.759
0.13710	1.780	1.773
	Average, 1.750	1.736

Below are tabulated several results of carbon disulphide determinations in benzene samples, 90 and 100 per cent., by the method derived from the data secured in the above experiment.

RESULTS OF ANALYSES BY THE METHOD DESCRIBED.

Sample No.	Determination. I.	II.	Difference.
1	0.809	0.765	0.044
2	0.475	0.477	0.002
3	0.442	0.414	0.028
4	0.743	0.764	0.003

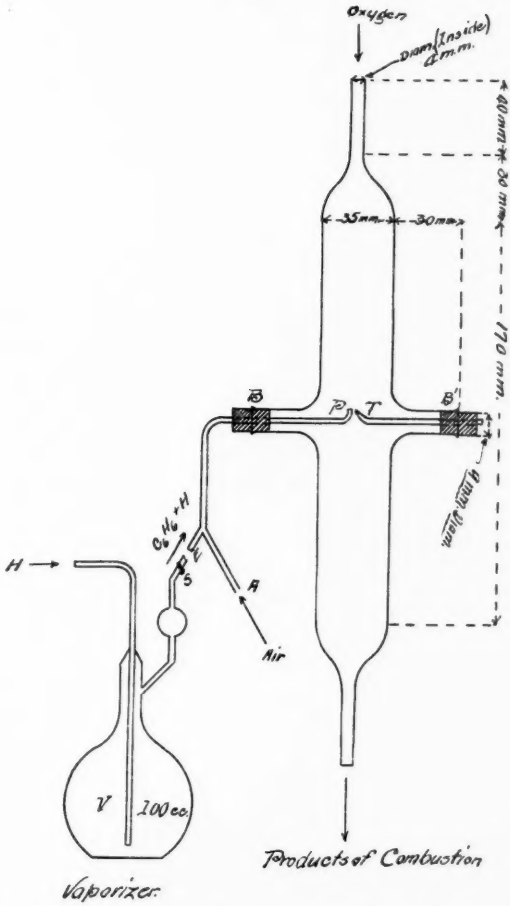
II. DETERMINATION OF TOTAL SULPHUR IN BENZENES.

The determination of total sulphur in benzene by the usual method of Carius for organic compounds is wholly impracticable. Acting in part on suggestions extant, as a result of the work of the older and more recent investigations in this field, it was sought to accomplish the purpose by vaporizing the hydrocarbon and combustion of the gas-mixture in an atmosphere of oxygen. The products of the combustion were passed into a suitable absorption medium and determined by familiar methods. The experimentation here involved related especially to a *form of apparatus* well adapted to the combustion and resulted in the vertical combustion-tube described in the immediate context. It was further made to embrace several features concerning the absorption and determination.

1. The Apparatus.

The hydrocarbon is contained in a small flask of about 100 cc. capacity of the form shown in the sketch accompanying at *V*. It is connected at *H* with a supply of sulphur-free hydrogen. The outlet beyond the stopcock *S* is connected with the Y-tube attached to the arm *B* of the combustion-tube. The bulb on the exit-tube serves to prevent the spurting of condensate into the burner, which becomes possible when heat is required to assist the vaporizing.

The combustion-tube is shown in the essential features in the sketch. The Y-tube *E A* carries the burner, as seen, at *P*. The latter is a platinum piece slipped gas-tight over the glass tube. The burner-tube is joined by a short piece of rubber tubing to the arm *B*. At *T* is the tip for the pilot-flame. It is likewise of platinum, and is fused into a glass carrying-tube in the position indicated. In each arm, but not shown in the drawing, is a coil of platinum foil. It extends from the stopper nearly to the center of the combustion-tube. The arm-space is filled as completely as possible, only room required for the free passage of the burners being left. The upper end of the combustion-tube is connected



Vaporizer.

with the oxygen supply. The gas is passed for purification through a calcium chloride tower filled with pieces of caustic soda. Beside this jar stands a second charged in the same manner and serves for the purification of the air forced in at *A*. The connections on the jars are such that at the end of the combustion air may be turned into the apparatus from above, through the oxygen jar, for the purpose of aspiration, without disconnecting at any point.

The hydrogen for the pilot-flame is purified by passage through a small wash-bottle containing a solution of caustic soda. The arrangement is further required in aiding the regulation of the flow of gas. To observe the rate of the oxygen supply and deliver it comparatively dry to the purifying apparatus, thus prolonging the serviceability of the latter, the gas passes from the holder first through glycerol.

The combustion-tube is wrapped in asbestos cloth for protection against drafts, a small opening only being left opposite the flames to permit of their observation. In the coolest part of the tube, the arm, a dangerous accumulation of water may take place. Warming becomes therefore necessary and is efficiently and automatically accomplished by the rolls of platinum foil already referred to. In this form the gas combustion-tube has proven itself well adapted to its purpose; the cracking of the tube in service is rare and then usually the result of inadvertence.

2. The Combustion.

The sample of benzene, about 5 grams, having been weighed in the vaporizer and all connections established, the apparatus is first filled with oxygen. The pilot-flame tube is withdrawn, a small flame started and the burner returned to its position in the combustion-tube. When first inserted, the flame must be larger than it is expected to maintain it, otherwise by the pressure existing in the tube, it will be so reduced in size as to be extinguished by the draft in the apparatus. The flame is adjusted to the smallest possible size consistent with keeping it alive. Care is taken to so place it that it is close to the edge of the burner-tip and will thus ignite the vapors instantly upon their arrival. With the arm *A* of the burner-tube and the stop-cock *S* closed, the hydrogen is turned into the vaporizer and thence cautiously admitted to the burner. Due to the downward movement of the oxygen, the vapors ignite even before reaching the tip of the burner, if the rate of admission is a little too slow. The flame appears at the tip brilliantly luminous. Increasing its size somewhat, air is admitted and the combustion continued with a half-luminous flame about 1 inch in length. Since some variation in the pressure of the gas entering the burner is scarcely to be avoided, the operation requires some oversight. The complete disappearance of benzene from the

gases supplied to the burner may be sharply detected by the appearance of the flame. A perfectly non-luminous flame denotes with certainty the end of the combustion. The stop-cock *S* is then closed, the pilot-flame extinguished, the oxygen turned off, and the passage of air through *A* continued for a few minutes. *A* is then closed and the air turned into the upper end of the combustion-tube by the simple setting of the stop-cocks on the air and the oxygen drying jars.

The combustion of 5 grams of benzene may be accomplished in about three hours. This applies to 90 and 100 per cent. benzene; light oil, with its less volatile constituents, requires a longer period. Warming the vaporizer hastens the operation and is necessary to completion of the process within a reasonable time.

3. The Absorption.

The gases and vapors leaving the combustion-tube contain the sulphur of the sample mainly as sulphur dioxide, but doubtless contain some sulphur trioxide as well. Mabery[1] states that in the form of apparatus devised by him for a somewhat similar purpose, the sulphur is contained wholly as sulphur trioxide notwithstanding the combustion was carried out in air, with the latter, however, in enormous excess. Special tests upon the gases from the above combustion apparatus detected sulphur dioxide unmistakably in large quantity. Several of the familiar absorbing media for the sulphur oxides were experimented upon and brominated sodium carbonate adopted for gravimetric determinations. The much more expeditious volumetric method of Mabery,[2] who used fractional normal alkali for absorption, was made the subject of some experiments.

In all cases glass-stoppered wash-bottles of about 250 cc. capacity were employed as receptacles for the absorber. Two were found adequate to the ordinary purpose.

The *sodium carbonate* and *bromine mixture* for absorption contained 25 grams of the purified crystallized salt dissolved in 110 cc. of water. The solution was distributed in equal volume between the two bottles. To the first was added more than an excess of bromine in saturated aqueous solution to oxidize the whole of the sulphur to be absorbed, assuming it present entirely in the form of sulphur dioxide. Ten cc. of the bromine solution

[1] Am. Ch. J. 18, 211.

[2] Pr. Am. Acad., Vol. 30.

are abundant for percentages up to 1.0. In each succeeding bottle of the absorber one-half the above quantity suffices.

With the carbonate-bromine absorber, as with all others tried, the formation of white fumes in the atmosphere of the absorbing bottles is a matter well-known to those who have dealt with the problem of the oxidation and absorption of the sulphur oxides, but perhaps still calling for some comment in this connection.

In all cases the fuming was most marked at the beginning of the combustion, at a time therefore when the vapors were most highly charged with sulphur in the form of carbon disulphide. Further, the higher the percentage of sulphur, the more voluminous the fume-formation, confirming the conclusion from the first observation that the fumes are carriers of sulphur. The subject is mentioned thus in some detail as emphasizing the necessity of a complete suppression of the fumes within the absorber if the utmost accuracy is to be attained. The accomplishment of this refinement, with conditions as set forth, has as yet not been fully realized in any simple manner. The limited and intermittent work which it has thus far been possible to devote to this phase of the determination has shown that, with an absorber made up of as many as four wash-bottles and with benzene samples of about 0.50 per cent. carbon disulphide, in the third and fourth bottles as a rule, the quantity of sulphur absorbed is practically the same, and an amount corresponding to somewhat less than 1 mg. of barium sulphate. Although numerous other devices (than increasing the number of absorbing bottles) for the promotion of extent and time of contact by the combustion gases with the absorber have been applied in conjunction with most of the practically available absorbing reagents, little or no better results than just indicated have been obtained. For technical purposes, however, this efficiency fully satisfies all requirements. The loss of sulphur sustained, by the use of two absorbing bottles as practiced, is not greatly beyond the limit of experimental error.

The use of N/50 *sodium hydroxide* gave, in the analysis of the 90 and 100 per cent. benzenes first experimented with very satisfactory results. Later efforts to apply the method to crude benzenes were unsuccessful. Time has not yet been available to determine the point of difficulty. The absorbing apparatus was composed in this instance likewise of two bottles each charged

with alkali in excess to the extent of 15 to 20 per cent. of the possible maximum requirement. Usually, about 0.5 cc. of the N/50 sodium hydroxide in the second bottle was used, and represents 0.003 per cent., with a total percentage, as above, of about 0.40.

4. Determination of the Sulphur.

The *gravimetric* determinations were made with the usual precautions current for accurate work.

For the *volumetric* method, as already stated, N/50 sodium hydroxide was contained in the absorbing apparatus. To determine the excess of alkali N/10 sulphuric acid was found most practicable. Since the sulphur is present partly as sulphite, before titration the solution was treated with a few cubic centimeters of neutralized hydrogen peroxide; 5 to 6 cc. of a 2 per cent. solution sufficed for the main portion. The contents of the second bottle were treated with half the amount. The titrations were made in the absorption bottles, and with methyl orange as indicator.

However determined, attention need scarcely be called to the necessity of recovering the sulphuric acid remaining after the combustion upon the walls of the tube. When special accuracy is an object, the residues left in the vaporizer, especially by crude benzene, become a consideration.

5. Comparison of the Results Obtained.

The results in the table following were from combustion of the same sample of benzene and, as noted, by both methods of determination.

GRAVIMETRIC AND VOLUMETRIC DETERMINATIONS COMPARED.

	Method.		
No.	Grav.	Vol.	No.
2	0.379	0.376	8
3	0.350	0.345	9
4	0.378	0.379	10
5	0.370	.....	...
6	0.370	.....	...
Average,	0.370	0.367	

Very satisfactory determinations have also been made with benzene containing as much as 5 per cent. carbon disulphide, the results being concordant within 0.10 per cent.

Insuring perfect and convenient combustion, the apparatus could be extended in its application to the determination of total sulphur in gases and vapors of whatever description. Fuel and illuminating gases are here in mind. It could further doubtless be made to lend itself in many instances advantageously to sulphur determinations in the ultimate analysis of organic compounds.

LABORATORY OF THE SEMET-SOLVAY CO.,
SYRACUSE, N. Y.

THE SYSTEM LIME, GYPSUM, WATER, AT 25°.[1]

BY F. K. CAMERON AND J. M. BELL.

Received June 30, 1906.

THE three-component system—lime, sulphuric acid, water—has been studied in this laboratory by Cameron and Breazeale.[2] In this work the composition of solutions containing an excess of the acid has been investigated over a wide range of concentration. In all solutions up to 300 grams of SO_3 per liter the stable solid phase is gypsum. We have investigated the composition of solutions in which the lime has been in excess of the acid.

Two series of solutions have been prepared, one, various lime solutions to which solid gypsum has been added, and the other, various gypsum solutions to which lime has been added. These bottles were put in the thermostat at 25° and were rotated constantly for a period of two weeks. At the end of this time known volumes were analyzed for lime and for sulphuric acid. These results are given in the following table:

TABLE I.

SO_3 per liter. Grams.	CaO per liter. Grams.	Solid phase.
0.0	1.166	$Ca(OH)_2$
0.230	1.302	"
0.392	1.424	"
0.562	1.608	"
0.714	1.742	"
0.934	1.876	$Ca(OH)_2$, $CaSO_4.2H_2O$
0.961	1.612	$CaSO_4.2H_2O$
1.013	1.320	"
1.090	1.112	"
1.128	0.966	"
1.194	0.898	"
1.251	0.875	"

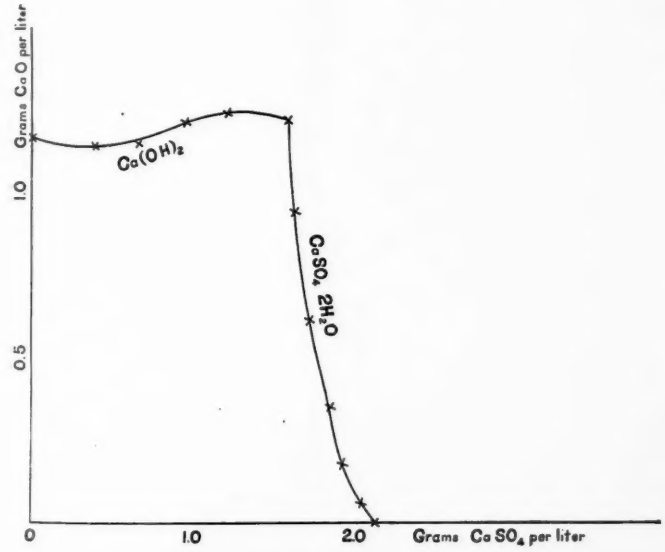
[1] Published by permission of the Secretary of Agriculture.

[2] J. Physic. Chem. 7, 571 (1903).

The results in the above table have been calculated to the amounts of calcium sulphate and of lime in the solution and are given in Table II. They are charted in the accompanying diagram.

TABLE II.

$CaSO_4$ per liter. Grams.	CaO per liter. Grams.	Solid phase.
0.0	1.166	$Ca(OH)_2$
0.391	1.141	"
0.666	1.150	"
0.955	1.215	"
1.214	1.242	"
1.588	1.222	$Ca(OH)_2$, $CaSO_4.2H_2O$
1.634	0.939	$CaSO_4.2H_2O$
1.722	0.611	"
1.853	0.349	"
1.918	0.176	"
2.030	0.062	"
2.126	0.0	"



These figures indicate that the solubility of lime in gypsum solutions is constant within a few per cent., the solubility being greater in the more concentrated solutions. In lime solutions,

however, the solubility of gypsum decreases regularly as the amount of lime in solution increases.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE PHOSPHATES OF CALCIUM, III; SUPERPHOSPHATE.[1]

BY F. K. CAMERON AND J. M. BELL.

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IN former papers[2] from this laboratory, the three-component system—lime, phosphoric acid, water—has been investigated at 25°. It was found that there are three solubility curves, one representing solutions in equilibrium with monocalcium phosphate, ($CaH_4(PO_4)_2.H_2O$), one representing solutions in equilibrium with dicalcium phosphate, ($CaHPO_4.2H_2O$), and the third representing solutions in equilibrium with a series of solid solutions. The compositions of these solid solutions extend from pure lime to a solution of nearly the same composition as dicalcium phosphate. Another three-component system—lime, sulphuric acid, water—has been studied in this laboratory.[3] The composition of solutions which are acid, *i. e.*, those in which sulphuric acid is in excess of lime, has been published in the former paper, while the composition of solutions which are alkaline has been investigated in the second paper. Only one solid phase was found in this first investigation, *viz.*, gypsum ($CaSO_4.2H_2O$). Had that investigation extended to more concentrated solutions of sulphuric acid, another solid phase, anhydrite ($CaSO_4$), would undoubtedly have been found. In the case of the alkaline solutions, two solid phases were found, calcium hydroxide and gypsum. In solutions containing less than 1.22 grams of free lime per liter the solid phase was found to be calcium hydroxide.

This present investigation deals with the four-component system—lime, phosphoric acid, sulphuric acid, water—the essential constituents of the so-called "superphosphates."

A complete representation of the conditions obtaining in any four-component system can be attained only by the use of a space

[1] Published by permission of the Secretary of Agriculture.

[2] Cameron and Seidell: This Journal; **27**, 1503 (1905); Cameron and Bell: Ibid., **27**, 1512 (1905).

[3] Cameron and Breazeale: J. Physic. Chem. **7**, 571 (1903); Cameron and Bell: This Journal, **28**, 1220 (1906).

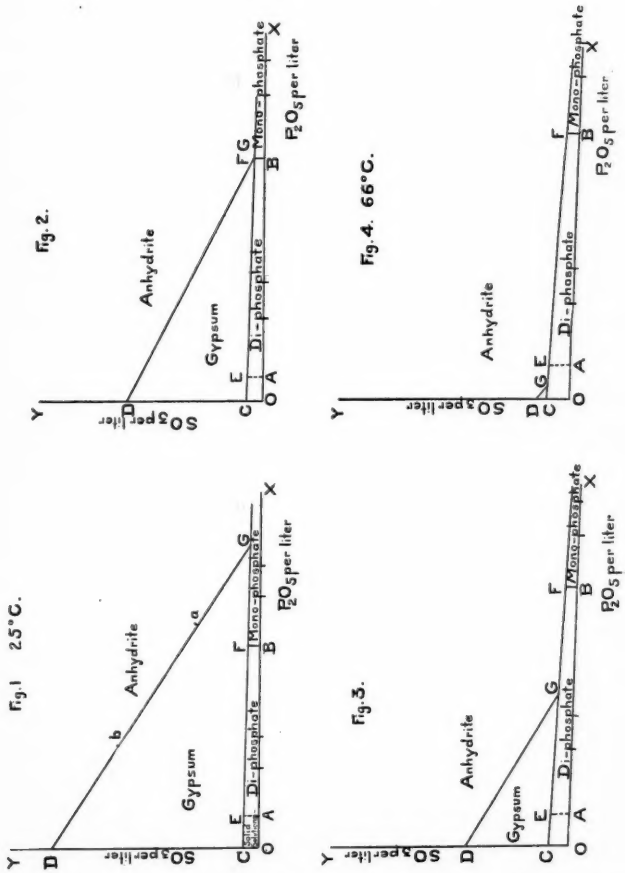
model. Such a space model for this four-component system, would have as axes, the amounts of lime, sulphuric anhydride, and phosphoric anhydride per liter of solution. With the densities known, the amount of water in these solutions can be computed. However, this representation is cumbrous and so we have represented the results on one of the projections of this space model, *viz.*, on the coordinate plane bounded by the SO_3-axis and by the P_2O_5-axis. In other words, we have used a plane diagram representing all the conditions, with the exception of the lime content of the solutions. These conditions are described in the accompanying diagram (Fig. 1), in which some of the fields are so narrow as to necessitate their distortion in order to show plainly the regions involved.

In (Fig. 1) O represents a saturated solution of lime in water. On the OX axis, A represents the solution in equilibrium with dicalcium phosphate and the limiting solid solution; B represents the solution saturated with respect to both dicalcium phosphate and monocalcium phosphate. On the other axis, C represents the solution saturated with both calcium hydroxide and gypsum, and D the solution in equilibrium with both gypsum and anhydrite. The positions of the points A, B, C have been found by direct experiment, while the position of the point D has been determined in an indirect way. This method was adopted, since the change of gypsum to anhydrite, or *vice versa*, has been shown to be very slow. In his work on the various forms of calcium sulphate, van't Hoff[1] has shown that at vapor-pressures lower than 17.5 mm. at 25°, gypsum is transformed to natural anhydrite, and above that pressure the reverse change takes place. Applying this result to the present problem, we have determined the strength of sulphuric acid which has a vapor-pressure of 17.5 mm. when saturated with gypsum. The sulphuric acid solution having this vapor-pressure has been found, from the results of Richards,[2] to have a density of 1.235. This solution contains 25.71 per cent. SO_3,[3] or 317.5 grams SO_3 per liter. In this consideration no correction is made for the effect of the calcium sulphate in solution on the vapor-pressure, a correction which would be very small because of the low solubility of gypsum in sulphuric acid

[1] Sitzungsber. Akad. Wiss. Berlin, 1901, 1140.

[2] Pr. Am. Acad. 33, 23 (1897-98).

[3] Fresenius "Quantitative Analysis," 1899, p. 676.



of that strength. This solubility has been estimated by extrapolation from the results of Cameron and Breazeale[1] to be approximately 1 gram of calcium sulphate per liter of solution.

The determination of the possible fields has been investigated by adding small quantities of sulphuric acid to various solutions epresented on the diagram by points on the line OX. In all cases the addition of a little sulphuric acid causes a white precipitate which upon microscopic analysis proved to be gypsum.

[1] Loc. cit.

This indicates that the fields over which the phosphates of calcium can exist are very narrow indeed. An analysis for sulphates was made of three of these solutions, one about midway between A and B in the diagram, one very near B, and the third on BX. The sulphuric acid content of these three solutions was found to be 0.9, 0.6 and 0.3 gram SO_3 per liter respectively, and hence the line C E F G lies very close to OX, the two lines converging as we pass to the right. Analyses of some of these solutions have been made by Cameron and Seidell,[1] their lime content and phosphoric acid content being practically the same when no gypsum is present as it is when the solution is saturated with respect to gypsum. These solutions lie on the line E F, near the point E. Thus it is evident that the presence of gypsum has no appreciable effect on either the lime content or the phosphoric acid content of the solutions, and as the amount of the sulphate in solution is greater in this region than it is farther to the right, it is apparent that the solutions near F and to the right of F have the same lime content and phosphoric acid content as those on the axis OX. The positions of the points E and F have therefore been taken as almost identical with the positions of A and B.

Finally, the position of the line forming the boundary between the gypsum and anhydrite fields has been found. From the work of van't Hoff, which has been cited above, the vapor-pressure at which gypsum and anhydrite remain in equilibrium at 25°, is 17.5 mm. Consequently, the solutions on the diagram which have that vapor-pressure are on the boundary line between the two fields. In these determinations we have not attempted to obtain equilibrium conditions but we have found whether various solutions had vapor-pressures above or below this value. This has been accomplished by placing a weighed solution (25 grams of solution in a weighing-bottle) known to have this vapor-pressure in a bottle containing the unknown solution. After a time the former solution was again weighed, and from the loss or gain it has been found whether the vapor-pressure of the unknown solution was above or below 17.5 mm. In this way the position of the point G has been determined, at which point gypsum, anhydrite and monocalcium phosphate co-exist as solids in equilibrium with a solution. Also we have found the position of two points,

[1] This Journal, 26, 1461 (1904).

a and *b*, along the line D G which separates the gypsum field from the anhydrite field.

To determine the point G various solutions along BX, whose vapor-pressure are not different from those along F G, have been investigated with the following results: The solution containing 485 grams P_2O_5 per liter caused an increase in weight of 0.080 gram in two days; the solution containing 563 grams P_2O_5 per liter caused a decrease in weight of 0.026 gram in two days. As these experiments were carried on under identical conditions, we have interpolated to find that solution which should show no change in weight. This has been found to contain 545 grams P_2O_5 per liter, and therefore G is determined. The positions of the points *a* and *b* have been found by similar pairs of determinations. The composition of the solution at *a* is 350 grams P_2O_5 per liter and 120 grams SO_3 per liter, and the composition at *b* is 150 grams P_2O_5 per liter and 275 grams SO_3 per liter.

The following table gives the data concerning the invariant or "constant" solutions at 25°.

Point.	P_2O_5 per liter. Grams.	SO_3 per liter. Grams.	CaO per liter. Grams.	Solid phases present.
O	0	0	1.17	$Ca(OH)_2$.
A	3	0	1.5	Solid solution; $CaHPO_4.2H_2O$.
B	317	0	77.	$CaH_4(PO_4)_2.H_2O$; $CaHPO_4.2H_2O$.
C	0	0.9	1.9	$Ca(OH)_2$; $CaSO_4.2H_2O$.
D	0	317.5	1.	$CaSO_4.2H_2O$; $CaSO_4$.
E	3	0.9	1.5	Solid solution; $CaSO_4.2H_2O$; $CaHPO_4.2H_2O$.
F	317	0.6	77.	$CaSO_4.2H_2O$; $CaHPO_4.2H_2O$; $CaH_4(PO_4)_2.H_2O$.
G	545	0.2	38.	$CaSO_4.2H_2O$; $CaSO_4$; $CaH_4(PO_4)_2.H_2O$.

To describe the conditions which obtain at any other temperature than 25° it is necessary to determine how the various points on the diagram are affected by changes of temperature, and also to determine whether any new solid phases appear. In the present case a microscopic examination of the crystals formed at the higher temperature has revealed no new types and it is therefore probable that there are no new solid phases. Above the temperature 66° the solid gypsum, stable at all lower temperatures, becomes unstable and therefore does not appear on the diagram representing the conditions at 66°. It has been found by experiment that the points B and F move to the right with rising temperature. In other words the two phosphates of calcium co-exist in solutions which become richer in phosphoric

acid as the temperature increases. The points E and A have not been investigated at any temperature other than 25°, but it is certain from qualitative experiments that at higher temperatures there is a field for solid solutions just as there is at 25°. This has been indicated in Figs. 2, 3 and 4 by the dotted line E A. The direction in which the point D moves with change of temperature can be predicted from the results of van't Hoff[1] upon the vapor-pressure at which gypsum and anhydrite exist in equilibrium.

The composition of sulphuric acid solutions which have the same vapor-pressures at 10°, 25° and 35° have been computed from the data upon the vapor-pressures of these solutions,[2] with the following results. It is apparent that the point D approaches C with rise of temperature.

Temperature, °C.	Vapor pressure at which gypsum and anhydrite co-exist.	Composition of H_2SO_4 with same vapor-pressures in per cent. H_2SO_4.
10	5.79	37.6
25	17.5	31.5
35	32.2	28.5
66	150.	0.

At 66° gypsum and anhydrite co-exist in contact with their own solution in water. The presence of lime, whose solubility in water at this temperature is less than 1 gram per liter, will lower this temperature very slightly. Similarly along the line C E G F, the point G is continually moving towards the point C. Consequently, it is evident that the field for gypsum disappears at a temperature of 66° and anhydrite becomes the stable solid over a very great range of solutions.

It is evident that at some temperature intermediate between 25° and 66° the point F, which is moving to the right with increasing temperature, will meet the point G which is moving to the left. At this point we have a sextuple point, or six phases, vapor, solution, and the four solids anhydrite, gypsum, mono- and dicalcium phosphates. This state of affairs can exist at only one temperature and one vapor-pressure. This is shown diagrammatically in Fig. 2. As the temperature increases still further, the points D and G approach C, and Fig. 3 illustrates the state of affairs at some temperature below 66°. At the temperature 66° the field for gypsum disappears altogether.

From the preceding results and diagram (Fig. 1) the effect of

[1] Loc. cit.

[2] Landolt and Börnstein: Phys.-Chem. Tabellen (1905), pp. 166–167.

water upon a mixture of the salts may be deduced. We shall neglect in the following consideration the effect of substances other than gypsum and monocalcium phosphate, which substances are nearly always present in commercial superphosphates, *viz.*, ferric phosphate, aluminum phosphate, calcium chloride or fluoride, etc. All these substances will have some influence upon the positions of the various points and lines in the above diagram but if their amount is small we may neglect their influence. Let us leach a superphosphate composed of gypsum and monocalcium phosphate at 25°. The addition of water to monocalcium phosphate crystals causes a partial change to dicalcium phosphate and a solution saturated with respect to both phosphates. A small amount of gypsum will also pass into the solution. If water be added to this solution, or if the solution be drained away and fresh water added, more of the monocalcium phosphate will disappear and dicalcium phosphate will be formed. The net effect of this leaching is to wash out some free phosphoric acid, together with considerable quantities of calcium and a very small quantity of gypsum. If the addition of water is rapid, the time for this change may be very short indeed. During this change the composition of the solution is represented by the point F of Fig. 1, and if equilibrium conditions are obtained, the composition of the solution will remain constant until *all* the monocalcium phosphate disappears. It will be observed that the greater part of the original calcium phosphate has been removed. This may be partially represented by the equation

$$CaH_4(PO_4)_2 = CaHPO_4 + H_3PO_4,$$

all the phosphoric acid in excess of the compound $CaHPO_4$ being leached away, together with a considerable amount of the diphosphate, which is dissolved. Upon the removal of some of the solution and dilution of the residue by fresh water, the composition of the leachings will change rapidly until the point E is reached. Here another change takes place, the crystalline dicalcium phosphate giving up phosphoric acid, which carries some of the phosphate into solution. The solid changes to a solid solution of lime and phosphoric acid and upon continued leaching this solid solution changes gradually to that solid solution which in saturated gypsum solutions dissolves unchanged, *i. e.*, the ratio of lime and phosphoric acid which have gone into solution is the same as in the solid solution. Over this range of concentrations

gypsum has a much higher solubility and it will probably disappear before the solid solutions have all disappeared.

We may therefore divide the process of leaching of superphosphate roughly into four stages: First, monocalcium phosphate disappears, and solid dicalcium phosphate and a solution of phosphoric acid containing much of the lime are formed. The weight of the resulting dicalcium phosphate is less than one-half of the original monocalcium phosphate. Very little gypsum has gone into solution at this stage. The second stage consists in the complete change of dicalcium phosphate into an amorphous solid solution, and very much more gypsum goes into solution. The third stage in the leaching process is the gradual change in the solid solution to one containing relatively less phosphoric acid and more lime. The liquid solutions are now quite dilute and consequently gypsum will dissolve freely, and it is certain that the gypsum will all be washed away before the calcium phosphate (as solid solution) has been all dissolved. The fourth stage consists in the slow solution in water of a relatively insoluble solid solution of lime in phosphoric acid, which contains relatively more lime than would be required by the formula $Ca_3(PO_4)_2$.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE COMPOSITION OF THE DRAINAGE WATERS OF SOME ALKALI TRACTS.[1]

BY FRANK K. CAMERON.

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IN the reclamation of an alkali tract the analysis of the drainage water is the most ready method of following the changes taking place within the soil. That the nature of the drainage water and the changes which it may undergo are problems of great practical importance is obvious when it is considered that agricultural plants display such marked difference in their tolerance of different salts and salt mixtures in their nutrient media. It is also important to note that a study of drainage water not only furnishes a clue to the nature of the soil solution in the land from which it flows, but that it may have an important bearing on the management of neighboring lands upon which it may be desirable

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to use the water again for irrigation or where the land may be affected through seepage.

It has popularly been supposed that the composition of a drainage water from an alkaline soil could be easily predicted from a knowledge of the respective solubilities of the salts composing the alkali, and even the recent literature contains discussions of this subject based upon the erroneous notion that the several components of a mixture will necessarily be removed in the order of the individual solubilities. That such is not the case, but that the relation of the vapor-pressures of the solution and of the solid components, the formation of new molecular species (such as so-called double salts), as well as some other possible factors in each individual case, must be considered, has been known, though generally ignored, by chemists and soil investigators. That the composition of the resulting solution with respect to the dissolved constituents remains constant so long as no one of the solid components disappears is well illustrated in a simple case, a mixture of sodium nitrate and potassium nitrate. If such a mixture be treated by successive portions of water, assuming, of course, that the temperature be kept constant, the composition of the several resulting solutions will be exactly the same so long as both solid salts remain in the mixture. Precisely the same sort of thing will happen with any mixture of solids, no matter how complex the course of the washing out of a mixture of salts by water, the composition of the solution which results will depend only on the solid phases which are present and not on their relative amounts. When any one of the solid phases becomes completely washed out, the composition of the solution will change.

The accumulation of alkali at the surface of soils is due mainly to the evaporation of seepage waters from lower levels. These seepage waters will in all probability have a constant composition as the water has become saturated with respect to all the constituents of the salts in the lower depths. In the converse process of washing out, the solution should have a constant composition until some one or more of the salts completely disappears. This has actually been observed in the investigations of this Bureau.

A tract of land near Salt Lake City, Utah, has been under process of reclamation, tile drains having been installed and the land leveled and frequently flooded. When reclamation was

undertaken, the surface soil of this tract contained, on the average, upward of 2.7 per cent. soluble salts, while it now contains less than 0.3 per cent. soluble salts. At frequent intervals since the installation of the drains, samples of the water from the outlet weir of the drainage system have been forwarded to the laboratory for analysis. The composition of the principal dissolved mineral constituents, at several different dates, is given in the following table, the analyses up to September, 1904, having been made by Mr. Bailey E. Brown, and the subsequent analyses by Mr. W. C. Taber.

TABLE I.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR SALT LAKE CITY, UTAH.

Date.		Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K. Per cent.	SO_4. Per cent.	Cl. Per cent.	HCO_3. Per cent.	CO_3. Per cent.	Parts per million in solution.
1902	Sep.	0.38	0.50	33.74	2.04	18.62	37.76	6.49	0.48	18035
	Oct.	0.23	0.78	34.73	1.49	19.14	39.52	5.06	0.29	17915
	Nov.	0.19	0.74	34.42	1.40	18.61	40.46	3.95	0.23	19905
1903	May	0.38	0.61	34.48	0.84	29.90	38.19	4.30	0.25	18752
	June	0.45	0.85	34.18	1.09	17.52	41.00	4.23	0.42	21099
	July	0.50	0.80	34.06	1.25	18.24	40.24	4.67	0.30	19089
	Aug.	0.35	0.90	34.40	1.12	17.15	42.37	3.48	0.16	26060
	Sep.	0.49	0.72	34.54	1.24	17.31	42.02	3.36	0.33	22240
	Oct.	0.47	1.02	33.43	1.52	16.08	43.28	3.33	0.30	19020
	Dec.	1.25	0.70	32.62	1.69	19.89	37.44	6.18	0.22	12966
1904	Jan.	0.15	0.75	33.93	1.26	20.08	36 64	6.94	0.25	11334
	Feb.	0.34	0.78	34.59	0.70	18.95	40.15	4.49	....	.....
	Mar.	0.29	0.77	34.57	1.28	16.31	42.28	3.81	0.19	21006
	Apr.	0.29	0.70	34.28	1.37	20.93	38.04	3.33	1.06	16372
	May	0.71	0.74	26.92	4.01	21.26	40.93	4 05	1.38	12677
	June	0.37	0.70	32.60	3.55	19.94	37.42	4.05	1.37	12695
	Aug.	0.37	0.86	33.85	2.13	17.12	41.31	3.20	1.16	15073
	Sep.	0.42	0.79	34.10	1.35	19.01	39.85	4.11	0.37	15717
	Oct.	1.04	0.60	33.01	1.86	21.42	36.63	4.68	0.76	11623
1905	Feb.	0.32	0.67	33.59	0.99	22.30	33.32	8.45	0.36	8235
	Mar.	0 31	0.66	33.46	1.30	21.60	33.86	8.46	0.35	8455
	Apr.	0.35	0.65	34.20	1.01	20.03	36.99	6.22	0.55	10701
	May	0.45	0.86	33.43	1.20	20.59	36.04	6.96	0.47	9569
	June	0.40	0.94	34.05	1.32	20.89	35.85	5.71	0.84	10612
	July	0.32	0.69	33.67	1.30	21.17	34.94	7.23	0.68	8763
	Aug.	0.35	1.04	33.12	1.58	21.58	35.92	5.72	0.99	9000
	Sep.	0.42	0.82	33.39	1.26	21.18	34.85	7 41	0.67	8992
1906	Jan.	0.55	0.84	33.12	1.11	21.10	34.35	8.57	0.36	8401
	Apr.	0.32	0.77	34.03	1.09	19.84	37.40	6.03	0.52	11531

It will be observed that the variations of the several constituents, within an interval of nearly four years, are very small,

such differences as do appear being readily attributable to the relatively small changes in the actual concentrations of the drainage water at different times, produced by the addition of large quantities of water in flooding, some of which reached the tiles before coming into equilibrium with the soil components.

In Tables II, III and IV are given the data obtained with drainage waters from a tract near Fresno, California, a tract near North Yakima, Washington, and a tract near Billings, Montana. In these cases it has not been considered necessary to have such complete analyses, over the entire time which the reclamation has been progressing, so that the data given apply to much shorter intervals than in the case of the Swan tract. They furnish, nevertheless, interesting examples of the same character.

TABLE II.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR FRESNO, CALIFORNIA.

Date, 1903.	Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K. Per cent.	SO_4. Per cent.	Cl. Per cent.	HCO_3. Per cent.	CO_3. Per cent.	Parts per million in solution.
March 28	8.90	3.77	11.78	2.66	12.23	6.66	54 00	.....	450
April 25	6.91	6.06	7.88	2.18	4.85	8.85	63.27	.....	824
May 2	3.59	4.15	16.35	1.75	2.39	8.95	60.99	1.83	1251
May 9	3.57	3.64	20.49	1.58	2.06	9.62	51.82	7.22	1454
May 16	3.58	3.76	19.72	1.44	1.88	9.69	54.79	5.14	1592
May 23	5.36	4.28	15.47	1.76	3.06	10.73	59.34	.....	1306
May 30	2.07	3.47	23.55	2.00	7.01	10.55	40.63	10.57	1639
June 6	3.01	3.15	22.84	2.35	6.45	11.79	40.50	9.79	1495
June 13	3.24	2.96	22.70	2.19	3.91	13.35	43.32	8.29	1048
June 20	3.81	3.21	21.82	1.87	2.79	11.78	54.19	.....	1494
June 21	3.20	3.38	21.09	2.82	2.63	9.88	56.96	.....	1062
July 4	3.06	2.27	20.82	2.63	4.98	6.12	57.21	2.97	1143
July 11	3.60	1.69	23.04	3.77	6.38	18.09	39.32	3.90	768

TABLE III.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR NORTH YAKIMA, WASHINGTON.

Date, 1903.	Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K. Per cent.	SO_4. Per cent.	Cl. Per cent.	HCO_3. Per cent.	CO_3. Per cent.	Parts per million in solution.
Aug. 1	4.93	5.26	12.91	4.09	20.06	4.85	47.91	.....	1440
Aug. 9	8.43	6.46	7.06	4.27	17.57	7.30	48.87	.....	1684
Aug. 15	7.58	3.23	14.19	4.68	24.51	6.47	36.95	2.40	2162
Aug. 22	7.57	5.03	12.09	3.37	23.68	6.45	39.10	2.66	2166
Aug. 29	5.27	5.06	14.52	3.56	21.36	4.79	41.43	3.96	1460
Sep. 5	7.36	5.21	12.38	1.86	23.33	5 01	43.40	1.38	2092
Sep. 12	9.32	5.59	10.29	1.32	25.55	6.79	41.12	trace	2575
Sep. 19	4.80	10.91	0.33	0.56	26.06	5.94	46.21	2.43	1768
Sep. 26	5.05	4.98	14.44	3.49	15.18	5.21	47.31	4.32	1343
Oct. 3	5.09	0.41	15.36	2.20	14.12	0.47	54.23	.....	1451

TABLE IV.—COMPOSITION OF SOLUBLE SALTS CONTAINED IN THE DRAINAGE WATER OF THE TRACT NEAR BILLINGS, MONTANA.

Date.	Ca. Per cent.	Mg. Per cent.	Na. Per cent.	K. Per cent.	SO_4. Per cent.	Cl. Per cent.	HCO_3. Per cent.	CO_3. Per cent.	Parts per million in solution.
1905 June	2.0	5.84	20.44	0.45	65.98	1.57	3.65	0.07	22376
July	2.33	5.71	20.29	0.53	65.27	1.60	4.27	.....	15490
Aug.	3.25	5.36	19.45	0.82	63.53	1.79	5.80	.....	7841
1906 May	3.63	5.95	18.72	0.46	69.07	1.47	0.45	0.25	11950

The data just presented are believed to be of more than ordinary importance, because they so well illustrate the character of the results which may be anticipated in a large number of cases in actual field work. How long the practically constant percentage composition of the dissolved salts would continue in the drainage water under continued flooding it is, of course, difficult, if not impossible, to predict. It is reasonably certain that sooner or later some one or more of the solid components in the soil would be completely removed, barring absorption or some other special phenomena, and the nature of the solution might then be very materially altered. As a practical matter, however, it should be remembered that the persistence of the several solid phases of the alkali mixture does not necessarily mean that they are evenly distributed in the soil, and that while they may be determining the composition of the solution as it passes into the drain tiles, some of these solid phases may have been removed from the surface soil, which would then hold a solution of different character, in which latter crops could very well grow. This seems to be true, as there is evidence that crops can now be grown on some of these tracts, if proper cultural methods be maintained to prevent the subsequent capillary rise of the water added in flooding. It appears certain, however, that in such cases the land can not be truly regarded as finally reclaimed until the change in the composition of the drainage water shows that there has been a complete removal of some of the solid salts from that portion of the soil which feeds the drains.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE LIBERATION OF FORMALDEHYDE GAS FROM SOLUTION BY MEANS OF ITS ACTION ON POTASSIUM PERMANGANATE.

By G. B. Frankforter and Rodney M. West.

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As indicated in this Journal (**27**, 714), when strong formaldehyde is brought in contact with powdered potassium permanganate, a violent reaction takes place liberating carbon dioxide, formic acid, a large amount of formaldehyde gas and producing a large amount of heat. Experiments extending over a number of years have been made with the object of determining the ratio between the amount of formaldehyde liberated and the amount of heat produced, or in other words, the amount of heat produced by the oxidation of a known amount of formaldehyde gas. The results of a large number of experiments showed that it is extremely difficult to obtain concordant results. It was found that the condition of the permanganate, whether in crystal form or whether coarsely or finely powdered, made a great difference in the reaction. The strength of the formaldehyde solution and the rate of flow upon the permanganate likewise made a great difference both in the percentage of formaldehyde liberated and in the amount of heat produced. In fact, so many variables entered into the reaction that the calorific determinations were laid aside for the time and the conditions under which the greatest amount of formaldehyde gas could be liberated by potassium permanganate studied.

DETERMINATION OF FORMALDEHYDE.

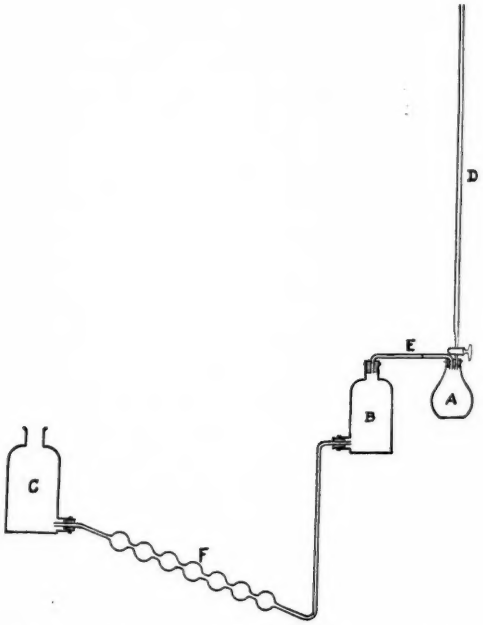
Several obstacles were encountered in the determination of the amount of formaldehyde gas liberated by means of potassium permanganate. One of the first difficulties was in retaining the formaldehyde gas so that it could be accurately determined. The evolution of gas is usually so violent that the ordinary gas-bag stop-cock is not large enough to allow the gas to escape without producing an enormous pressure upon the generator; or in case of absorption of the gas it is extremely difficult to absorb all the gas either by water or by ammonia.

Another difficulty was experienced in bringing the formaldehyde solution in contact with the permanganate. If the aldehyde is allowed to drop on the permanganate from a burette, a crater

of oxides of manganese is formed just where the aldehyde comes in contact with the permanganate, retaining the aldehyde so that after a short time the reaction almost stops. If, on the other hand, the formaldehyde is added all at once, the gas is liberated with explosive violence and at the same time the actual percentage of formaldehyde liberated is considerably less than when the formaldehyde solution is allowed to drop from a burette on the permanganate. In fact, several violent explosions were caused by adding strong formaldehyde solution to finely powdered permanganate. Frequently when 40 per cent. formaldehyde is slowly dropped on the powdered permanganate, a little flame is produced as each drop of formaldehyde strikes the powder. In this case the amount of formaldehyde is greatly diminished and the carbon dioxide greatly increased.

An attempt to overcome this violent reaction was made by diluting the formaldehyde with water. It was found, however, that while the addition of water modified the reaction, the quantity of formaldehyde gas was greatly diminished. Finally, the dilution of the permanganate by some inert substance was tried and found to give satisfactory results. The potassium permanganate was powdered and mixed with clean sand and the formaldehyde allowed to drop on this mixture. The sand prevented the formation of the crater of oxides of manganese. The formaldehyde percolated through the mixture and the reaction continued as long as the aldehyde was added and as long as there was unchanged permanganate left in the generator. As the gas is liberated from the solution by the heat of the reaction and as the specific heat of the sand is much less than that of water, more heat and hence more gas must necessarily be liberated by diluting the permanganate with sand than by diluting the formaldehyde solution with water. Notwithstanding the modifying effect of sand upon the above reaction, the change was still violent unless a large proportion of sand was used. It was found that a mixture of equal parts of sand and permanganate gave best results. With this proportion the reaction was violent but not to such an extent as to make the collection of the gas impossible.

Several forms of apparatus were tried. That indicated in Fig. 1 was adopted as giving satisfaction, whether the gas was collected in gas bags and measured or determined by absorption. A wide-mouth, short-neck flask *A* of about 200 cc. was fitted with



a double bored rubber stopper. Through one hole passed a burette for introducing a known quantity of formaldehyde. Through the other passed a delivery tube *E* of large diameter. This delivery tube was connected with an aspirator bottle *B* filled with water, one liter giving best results. The side neck of the aspirator bottle was connected with an absorption tube *F*. The absorption tube was so placed that the upper end was below the surface of the water in *B*, thus slightly diminishing the atmospheric pressure upon the gas. The other end of the absorption tube was connected with another aspirator bottle *C* which serves as a receiver in case the gas is not entirely absorbed as soon as it passes into *B*. If the reaction is very violent, forcing all of the water out of *B* into *C* by rapid liberation of gas, loss will be prevented by bubbling through the water in the absorption tube. At the end of the reaction the water is finally drawn back into *B*, but is prevented from being drawn over into *A* by the air which filled the generator at the beginning of the experiment. Usually,

the absorption-tube is unnecessary except as a connecting tube between *B* and *C*. When all the gaseous formaldehyde has been absorbed by the water, it is thoroughly mixed, measured and the formaldehyde determined. During the reaction the temperature in the generator is practically constant at the boiling-point of water.

In the following table of analyses the solution used was 37.8 per cent. formaldehyde and the permanganate used was mixed with an equal amount of sand. The quantity of water used in absorbing the gas was varied, but 500 to 1000 cc. seemed to give the best results when 50 cc. of the formaldehyde solution were used. With very large quantities of water the solution became so dilute as to make an exact determination of formaldehyde somewhat difficult

	$KMnO_4$ + Sand. Grams.	Formaldehyde solution. cc.	Volume of water used in absorption. cc.	CH_2O liberated. Per cent.
1	100	50	1000	69.12
2	100	50	1000	71.42
3	100	50	1000	69.12
4	100	50	1000	67.96
5	150	50	1000	65.92
6	150	50	1000	63.53
7	200	50	1000	71.77
8	200	50	1000	70.00
9	200	50	1000	70.00
10	200	50	1000	65.00
11	200	50	1000	65.00
12	200	50	500	64.53
13	200	50	500	64.53
14	200	50	500	64.53
15	200	50	500	67.43
16	200	50	500	67.53
17	200	50	500	64.53
18	200	50	500	62.21
19	200	50	500	64.53

A large number of determinations were made, varying the time of reaction or the rate of flow of formaldehyde solution on the permanganate. The following table gives the average percentage of gas liberated:

Number of analyses.	Time of reaction. Minutes.	CH_2O. Per cent.
3	80	65.96
3	60	68.06
6	45	73.11
3	30	74.56
2	15	73.56
9	10	70.48

In these determinations 200 grams of the mixture of sand and permanganate and 50 cc. of 38 per cent. formaldehyde were used. During the process a considerable quantity of water distilled over. The greater part of the water came from the formaldehyde solution; a small quantity was formed by the oxidation of the formaldehyde. Measurements showed that about 45 cc. distilled.

The above averages indicate that with the quantities of permanganate and formaldehyde used in these experiments, the best results were obtained by allowing thirty minutes to complete the reaction. When more than that is taken, the amount of formaldehyde liberated seems to decrease and the amount of carbon dioxide to increase. With less than thirty minutes to complete the reaction, the amount of formaldehyde decreases and the amount of carbon dioxide seems also to decrease. Determinations of both carbon dioxide and formic acid are now being made.

UNIVERSITY OF MINNESOTA.

NOTES.

A Modification of the Hanging Drop Fluoride Test.—The necessary apparatus consists of a test-tube of small bore and about 2 inches long (a litmus-paper bottle serves admirably), fitted with a rubber stopper. The latter carries a small bit of glass tubing, closed at one end and inserted in the bottom of the stopper so that the open end shall extend about 3 mm. into the tube.

The precipitate of calcium carbonate and calcium fluoride, ignited until nearly free from carbonate, is well mixed with about 0.1 gram of precipitated silica and introduced into the dry tube. The bit of glass tubing is nearly filled with a couple of drops of water, the bottom of the stopper wiped thoroughly dry, and the latter inserted into the tube immediately following the addition of 1 to 2 cc. strong sulphuric acid. Place the tube in a beaker of water at the boiling-point and maintain at this temperature for fifteen to thirty minutes. If the substance under examination contained any appreciable quantity of fluoride its presence will be promptly indicated by the formation of a heavy gelatinous ring that not infrequently completely fills the end of the tube in the stopper.

In the writer's estimation, this procedure is far preferable to the troublesome and occasionally somewhat uncertain etching

test usually employed. Furthermore, by simultaneously proceeding with tubes containing known amounts of fluoride, this process may be made roughly quantitative.

C. D. HOWARD.

The Disposal of Ammonia, Tar and Gas from By-Product Coke Ovens.—The writer's attention has been called to a review in the June number of the Journal, of the book entitled "A Short Treatise on the Destructive Distillation of Bituminous Coal," in which the reviewer draws some conclusions as to the disposal of coke oven by-products that hardly seem justified when the rapid development of these markets in recent years is considered, as well as their present status. The review questions whether the addition of a plant carbonizing 1,000 tons of coal daily, to the present by-product oven installation, producing approximately three and a quarter million gallons of tar and 3,500 net tons of ammonium sulphate per year, would not so depress the by-product market as to "deprive that type of construction not only in the new plants, but also in those previously erected, of the greater part, if not all, of the advantages resulting from its output of by-products."

The market for ammonia in all forms, including sulphate, has undergone an increase from 18,000 net tons of sulphate equivalent produced in 1899, to 54,664 net tons in 1904, or, roundly, 200 per cent. increase in five years. The average price has consistently risen during this addition and has shown to date no tendency to recede. As the imports of sulphate were 6,976 net tons in 1899, and 15,288 net tons in 1905, any apprehension as to a catastrophe in this particular industrial field by the addition of 3,500 tons to the home production may well be laid aside until needed. Such an installation as cited requires a year for its completion, which is ample notice for the market to adjust itself to requirements. To one who appreciates the vast field open to ammonium sulphate as a fertilizer, and who is aware that the United States, the greatest agricultural country in the world, now uses but one-third of the nitrogen used as a fertilizer in Germany, per unit of population, including the large nitrate of soda imports in both countries, such apprehensions seem idle.

The market for tar, it is true, furnishes more reasonable ground for conservatism. The tar from the 3,000 odd by-product coke

ovens now in existence in this country has practically all come on the market within the last ten years, there having been but 72 by-product ovens in 1895, according to Dr. Parker's report. The total production of coal tar from gas works and by-product ovens was 69,498,085 gallons in 1904, according to the same authority. Of this, 41,726,970 gallons or 60 per cent. was produced in the gas works, the balance, 27,771,115 gallons or 40 per cent. being produced in the by-product coke ovens; therefore the addition of the by-product coke oven tar to the existing gas works production represents at least 66 per cent. increase, besides that due to the extension of the gas production itself. As the Geological Survey reports above referred to were not issued as early as 1895, we have no accurate data on this point, but the report by Dr. Wm. B. Phillips in 1898 gives the production of tar in gas works for that year as 24,384,798 gallons. The amount in 1895 was assuredly less than this. Contrasting this figure, however, with the present production we see that an increase has taken place of approximately 200 per cent. up to and including 1904, and including 1905, it will approximate 250 per cent. increase. Under these conditions the value of the tar, quoted in 1898 at 3.7 cents per gallon by the above authority has fallen to 3.04 cents in 1904. This is a loss, to be sure, but it is by no means a serious one. It must be remembered that the first resort for the tar producers in a low market is to burn it as a fuel, for steam raising, etc., for which purpose it is equivalent to coal at a ratio of 5 pounds of tar for 8 pounds of coal. Therefore, where coal is worth $3.75 per net ton, tar can be burned with equal economy at a cost of 3 cents per gallon, or where coal costs $3.12, tar is worth 2.5 cents per gallon.

Even under the tremendous expansion that the coal tar manufacturing industry has undergone, prices in this country have never averaged as low as those prevailing in England and Germany. Nevertheless in these countries the by-product oven system is constantly gaining ground, and in Germany in particular is now far in the lead. A far greater proportion of the United States tar production goes into the manufacture of prepared roofing and for water-proofing than is the case in either of these other countries. A great and immediate increase in the tar production might conceivably so far modify these conditions as to cause American prices to approach the English figures,

but this would detract but little from the economic advantages of the by-product coke oven process.

It is therefore clear that, for both ammonia and tar, the market conditions are far from supporting any apprehension as to their immediate future. Both have shown a remarkable capacity for extension without resort to the less remunerative avenues of disposal, and the demand for both seems to be constantly on the increase.

As regards disposal of gas, it is said that the market for fuel and illuminating gas is now fully supplied. But the source of this supply is based on the constant consumption of coal or petroleum oil, barring the cases where natural gas is used. Therefore the question of supply rests on a constant outlay for raw materials. If a supply of completely or partially manufactured gas of higher quality can be offered to the gas companies at the same cost, or an equally good quality at a lower net cost than the existing method of raw material supply and manufacture comes to, they will inevitably turn to the new and more economical source. It is merely a matter of dollars and cents. And that these arguments are worthy of consideration and that such conditions can and do prevail, is attested to by the fact that a considerable number of American cities are now successfully using the gas from by-product coke ovens for all or a large part of their illuminating and fuel requirements. The fact that in nearly every case a continual increase in the gas consumption has made frequent extensions of the gas-making plant necessary, and that the lowering of the price of gas extends its use enormously, must also be given due consideration. There are few American cities that do not anticipate larger gas plants, lower gas prices and greater consumption in the near future.

For these reasons it does not appear to the writer that the immediate extension of the by-product coke oven industry will be fraught with disaster to the by-product markets. In the light of what has gone before, the future does not seem otherwise than most promising.

C. G. ATWATER.

REVIEWS.

RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.[1]

By John D. Pennock.

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In his address delivered before the Congress of Applied Chemistry, held in Berlin in 1903, Mr. Ernest Solvay drew a striking picture of the fall of the LeBlanc soda process before the more economical ammonia soda process, showing year by year from 1870 to the present the constant lessening of one and the constant progression of the other, until in 1903 the world's production by the ammonia soda process was 1,610,000 tons, and 150,000 tons by the LeBlanc, while in 1873, twenty years before, there were produced by the LeBlanc process 447,000 tons, and only 2,600 tons represented the yearly production of ammonia soda.

Though the production of soda ash was then greatly curtailed, the LeBlanc works by no means had to close their doors, for while by the ammonia process, soda ash could be produced at a much less cost than by the LeBlanc process, there was not so great a difference in the cost of caustic soda as made by the two processes, and while the chlorine, combined with the sodium, the fundamental reagent in both processes, appeared in the LeBlanc process as a decidedly valuable by-product in the form of bleaching-powder, in the ammonia process it appears as calcium chloride, a practically waste product.

Naturally there are many uses to which calcium chloride may be put and for which a small financial return may be obtained, such as a drying agent for air, for refrigerating purposes in the place of brine, for cooking solution in the canning industry, for wall plaster in the Cappon process, and the seasoning of Portland cement, etc., but the sum of all these uses amounts to but a very small percentage of the total calcium chloride produced.

Therefore the mainstay, the prop that has kept the LeBlanc works from utter ruin, is the by-product chlorine, available and salable at a good price in the form of hydrochloric acid or bleaching-powder.

While the ammonia soda process has completely captured the soda ash market, it was expected that electrolytic methods would soon take possession of the bleach market. This assumption was not immediately realized; it required the expenditure of much capital and the failure of many companies before success was achieved, and only within the last year or two could it with certainty be said that electrolytic caustic soda and bleach have been established for all time. But the returns for last year's business indicate that there are at least two factories in England

[1] Read at the Ithaca Meeting of the American Chemical Society.

making a profit, namely, the Castner Kellner Alkali Co. (mercury process), which showed a profit of $250,000 for 1905, and the Electrolytic Alkali Co. (diaphragm process), which claimed a profit of $30,000. While the success of these two companies proves that electrolysis of sodium chloride is commercially profitable, the comparison of the returns of these two processes is also indicative of the superiority of the mercury process over the diaphragm process. This superiority is likewise shown in Europe and in the United States.

Hasenclever, at the head of the LeBlanc process in Germany, takes a pessimistic view of the future of the LeBlanc soda industry. He claims one-half the world's production of bleach, 260,000 tons, is made by electrolytic processes.

	Electrolytic. Per cent.	LeBlanc. Per cent.
Germany produces bleach	65	35
England	18	82
France	19	81
United States	100	0
Austria	66	34

Hasenclever says the only hope of the LeBlanc process lies in the discovery of new uses for sulphate and on the growth of the new sulphur dye industry.

Kershaw, on the other hand, when he studied the financial return of $1,500,000 made by the United Alkali Co., of England, for 1905, puts a more rosy aspect on the future of the LeBlanc works, but he must remember that the profits of this company came not so much from soda ash, caustic and bleach as from the various other chemicals which they produce in addition to the regular products. He too, like Hasenclever, concludes that while there will be some business in soda ash and bleach, their chief profits will come from the manufacture of sulphuric acid, sodium sulphate, hyposulphite, sulphite and other sulphur salts which cannot be made by the processes of either of their rivals.

That but meagre profits are on the whole being obtained in electrolytic soda operations is indicated by the recent tendency the world over to divert the chlorine from bleach into various other lines where better prices may be obtained, such as tin crystals, pure hydrochloric acid by combustion of the chlorine and hydrogen, carbon tetrachloride, and mono- and dichlorbenzene.

The world is in search of a solvent that is cheap and at the same time non-inflammable for use in paints, rubber manufacture, wool washing, etc. Carbon tetrachloride possesses the necessary properties and consequently many investigators are at work endeavoring to devise some cheap method for producing it.

As carbon tetrachloride contains 92 per cent. of chlorine and chlorine can not be made at less than 2 cents per pound, the chlorine alone will bring the cost of carbon tetrachloride to at

least 30 cents per gallon, while the cost of the operation will be as much more.

By the Taylor electric furnace, carbon disulphide may be made in large quantities very cheaply, and with this by the old process, carbon tetrachloride may be more cheaply made than formerly.

Another outlet for electrolytic chlorine is monochlorbenzene, which is a good solvent, having a freezing-point of —45°, boiling-point of 132°, and sp. gr. of 1.1125, and which may readily be formed according to Beilstein by passing chlorine into benzene heated to 50–60° in the presence of aluminium chloride as a catalyzer.

L. E. Andes (*Chem. Ztg. March*, 1906), on studying the properties of mono- and dichlorbenzene, finds them to have very desirable properties as solvents. Dichlorbenzene distils at 173°; it leaves, on evaporation, no odor or residue. One hundred grams each of monochlorbenzene, dichlorbenzene and turpentine were exposed to the air for fifty hours; 14 grams of dichlor-, 80 grams of monochlorbenzene and 32 grams of turpentine had evaporated. Both mono- and dichlorbenzene can be mixed in all proportions with drying oils, and can often replace turpentine.

Carbonate saponification of fatty acids instead of caustic treatment of neutral fats is meeting with considerable favor in Europe and is quite extensively used, whereas in the United States, thus far, but little progress has been made in that line. It is undoubtedly destined some time to reduce very largely the use of caustic soda for soap-making. One inventor has recently suggested using the crude bicarbonate from the ammonia soda process before drying, but it would appear rather impracticable on account of the ammonia present in the bicarbonate, as it would require condensing apparatus to prevent ammonia loss, which the soap-maker would hardly like to undertake. But carbonate saponification has advantages, chief among them the following:

First, the glycerol need not be dragged through the entire process of boiling as in the saponification of neutral fats. Second, the yield of glycerol is larger. Third, saponification by carbonates is cheaper, as the price of carbonate of soda is much less than that of caustic soda. So far as the process of saponification is concerned, it is immaterial whether the fatty acids employed are obtained by the use of the autoclave, by high or by low pressure, or by the open-kettle methods, such as the sulphuric acid process, the Twitchell process, the fermentative fat-splitting process, or Krebitz', a lime method. The main point is that the fatty acids shall be pure and of high percentage.

The Frasch nickel ammonia process for the manufacture of caustic soda would parallel the ammonia process for carbonate of soda, but in addition to the expensive reagent ammonia, nickel is also required.

By this process nickel hydroxide is added to a saturated solution of ammonia and brine and upon agitation a nickel ammonium chloride separates out and the caustic soda is formed in solution. The double salt, after filtration, is treated with lime, the ammonia evolved and the nickel precipitated in the form of hydroxide ready for use again.

The enzymic fermentation process for the production of fatty acids, due to the work of W. Coustin and his co-workers, as carried out in a working trial in Berlin, has proved a success. The enzyme of the castor oil seed has proved most active. A mixture of 50 pounds cotton oil, 34.5 pounds castor oil seeds, 3.3 pounds water and 2.5 pounds acetic acid, at a temperature between 70° and 104°, showed after three hours 42 per cent., and in twenty-four hours 90 per cent. of fatty acids. This ready elimination of fatty acids and separation of glycerol combined with saponification with carbonates is of great importance to the soap industry.

By-product coke ovens thus far have been built horizontally, but the process of G. J. Arts, recently patented, makes use of a vertical retort. The retort is cylindrical and the heating flues encircle the retort spirally. The coal is charged in at the top and discharged continually, dropping at the bottom into a closed boiler containing water for quenching. A higher yield of by-products and a higher illuminating value for the gas is claimed for the process since the ascending gases pass through a continually cooling zone, whereas in the horizontal by-product oven the gas carrying its benzene illuminants and ammonia passes over a hot bed of coke at about 1000°, where a certain amount of the ammonia is decomposed and where benzene is broken down into naphthalene. Another important point claimed for the process is that the steam evolved from incandescent coke rising through the mass further reduces the sulphur and phosphorus in the coke and at the same time produces a certain amount of water-gas. (*J. Gas Lighting*, May 22, 1906, pp. 519.)

All England is greatly agitated at the present time over the smoke nuisance; the bringing of the offending industrial operator to the court of justice is a daily occurrence in the manufacturing districts.

The rapid development of the coke oven, the Mond and the Loomis-Pettibone producers supplying gas for gas engines and as a cheap domestic fuel, will in the future do much toward reducing the uneconomical and smoke-producing process of direct combustion fuel.

Over 150,000 boiler horse-power capacity of Loomis-Pettibone plants in connection with gas engines have been installed and are now in operation in this and foreign countries.

It is interesting to note that the Union Carbide Co., which thus far has had an entire monopoly in the carbide business, is likely to have a competitor in the Hartenstein process which is in

operation at Constantia, Michigan. By this process carbolite, the name given to the carbide of a stone or flint-like structure, is obtained, which is not objectionably porous, not so hygroscopic and does not yield the percentage of fines that the present carbide does.

The recent activity in the utilization of peat in this country has demonstrated that the briquetting of peat for fuel purposes cannot be economically done. The conversion of peat into gas in producers, and using the gas for power in gas engines, promises to be successful. Certain grades of peat are making a cheap quality of paper. At Capac, Michigan, with a plant working the patented process of C. Esser (Patents No. 690,363, December 31, 1901, and No. 771,202, September 27, 1904) satisfactory results are obtained.

Ethyl alcohol to be used in the arts may be obtained free from tax after January 1, 1907, and it will be necessary to use some sort of a denaturator. In Germany (Fifth International Congress für Angewandte Chemie, Vol. II, p. 560) denatured alcohol is classed as "complete" or "incomplete." To produce "complete" denaturation 2.5 per cent. of a solution made by 4 liters of wood alcohol and 1 liter of pyridine is added to 100 liters of alcohol. "Incomplete" denaturation is the treating of the alcohol for a certain specific use, for instance, alcohol for use in rubber goods, is treated with shellac; for celluloid with camphor, etc.

France uses wood alcohol which must contain 25 per cent. acetone and 2.5 per cent. of empyreumatic compounds. Also heavy benzene, 150° to 200°, and other substances for special purposes.

Austria uses the same denaturators as Germany.

Switzerland uses 2.9 per cent. of a solution made up of 70 per cent. acetone, 10 per cent. pyridine, 10 per cent. solvent naphtha and 10 per cent. of the last runnings of wood alcohol distillation.

The few chemical processes and problems which my limited time has permitted me to touch upon thus far dwindle into insignificance when compared with that subject which of late has occupied the attention of many investigators; namely, the "fixation of nitrogen" in a form suitable for fertilization of vegetable growths. One can with difficulty name a subject of greater importance for future generations of mankind as well as our own than that which has to do with the supplying of food for the rapidly increasing population of the world. Any process for the production of nitrogenous substances convertible into vegetable tissue when mixed with the soil, should be hailed with delight. The cost of manufacture by such a process may at the present be so great as to preclude operating in competition with the present sources of supply, but the time will certainly come, if the process is technically possible, when conditions will so change

that the costly process of to-day will be the cheap process of to-morrow. Many of the important industrial operations of to-day, founded on reactions discovered generations ago, were successfully established only after sufficient advance in engineering and the arts in general made them possible. The reaction often remains dormant until the accumulated thought and experience of patient investigators, who perhaps have failed, but nevertheless have added one link in the chain of experience, ultimately brings commercial success. Humphry Davy, seventy-five years ago, demonstrated the results of electrolysis of sodium chloride, but it was many years before the dynamo made it commercially profitable.

The rise of the ammonia soda process offers another example. The basal reaction of the process was placed by Fresnel in competition with LeBlanc's before the French Tribunal, but was rejected because at that time no method for the recovery of ammonia was known. From that time until 1863 a dozen or more investigators tried to produce a commercial process but failed, but by each succeeding failure knowledge was gained, which ultimately brought success in the Solvay process.

In creating luxuriant vegetable growths by fertilization it is impossible to say which of the constituents in a fertilizer is the most important, phosphoric acid, potassium or nitrogen. All three are perhaps equally important and at the present time available in large quantities, and for many years to come the extended areas of potash salts in Germany, and the recently discovered salts of France, will furnish the supply of potassium, and when these are consumed a process for the separation of potassium from feldspar will furnish the requirements of plant life for years after the Stassfurt or similar deposits have been exhausted. Search for potassium deposits in this country should not be abandoned. Though the Michigan company which put down a well in Wyoming in 1899 in search of potassium salts failed, further trials should be made; rather the goverment should drill wells, and if successful, obtain a rental of the mines as the German government is now endeavoring to do. Mr. Courtis (*Min. Ind.* 1904) claims the locations favorable for the discovery of potash salts are (1) Cady, Wyoming; (2) Magnesium Lake, Laramie Co., Wyoming; (3) Brown Springs, Cal.; (4) Death Valley, Cal.; (5) Bound Brook, N. J.; (6) Mt. Tom, Mass.

The fact that the waters of many of the alkali lakes contain 8 to 10 grams per liter of potassium chloride may indicate a deposit of soluble salts or the decomposition of insoluble silicates.

The United States, which imported from Germany 216,000,000 pounds potash in 1905, valued at $3,551,000, should sometime have its own source of supply; for the Kingdom of Prussia, which is endeavoring to secure control of the potash salt mines, and has recently offered $7,000,000 for one of the large mines,

will doubtless curtail the exportation and advance the price of the exported product to enable its own farmers to use larger quantities at lower prices.

No better service could be done by Congress for the good of the agricultural interests than to appropriate $1,000,000 for the prospecting of potash salts, which are undoubtedly to be found somewhere within the boundary of the United States. There is no chemical investigation whose successful operation would bring greater financial returns than the separation of potassium from the potash feldspars which are to be found in large quantities in this country.

As for phosphoric acid, the United States has an abundant supply in the deposits of rock phosphate of the Southern States, and in apatite, which is found in many places in considerable quantities.

But as to the supply of nitrogen we are not so fortunate. The syndicate formed for prospecting in the Western States for nitrates thus far has produced no appreciable amount. The deposits on the western coast of South America will be depleted before many years, possibly within 30, and the great nitrate combine, recently formed, is continually advancing prices, and before another generation has passed we shall have to resort to some other source of nitrogen for the soil.

Briefly referring to nature's methods of securing available nitrogen, we first note that electric discharges during storms undoubtedly form oxides of nitrogen which are carried to the soil by rain and combine with alkalies in the earth to form nitrates.

Another of nature's processes of nitrogen fixation is that discovered by a German farmer, Schultz, who observed that certain plants, clover, peas, lentils, etc., greedily absorb nitrogen, and accordingly initiated the practice of turning under the early crops of these products to furnish nitrogen for the following crops. The reason for the lentil's power to thus fix nitrogen was later, in 1874, found to be due to tubercles produced on the roots of the plant by microorganisms. Other plants do not have these tubercles and hence cannot assimilate nitrogen to the same extent. That the fixation of nitrogen is thus going on is acknowledged by all biologists.

The efficacy of barnyard manures, tankage, garbage and other highly nitrogenous fertilizers is due to the ready formation of ammonia through the influence of bacteria in the soil.

It is unnecessary in this connection to dwell upon the work of these microscopic agencies, one class of which, called the ammonifiers, breaks down the organic substance forming ammonia, which is eagerly seized by the nitrifiers, producing a synthetic reaction and forming with oxygen nitric acid which is immediately taken up by an alkali forming a nitrate, in which form it is readily assimilated by the plant.

But we will pass over these natural methods and take up the application of natural inorganic and artificially produced nitrogenous substances.

In the first class we have sodium nitrate at present found in only one part of the world, Chili, and produced by a process of leaching and purification, the entire output being controlled by the nitrate kings of England.

The production of this mineral is rapidly growing and it is expected that before many years the supply will be exhausted; for not only is the demand for it as a fertilizer increasing, but the production of nitric acid is constantly increasing, causing an additional drain upon the supply.

In the year 1905 the production of sodium nitrate amounted to 1,733,644 tons, three-quarters of which was used in fertilizers.

	1904. Tons.	1905. Tons.
Production of sodium nitrate	1,540,000	1,733,644
Shipments of sodium nitrate to Europe	1,179,500	1,192,120
Shipments of sodium nitrate to United States	265,766	353,177
Shipments of sodium nitrate to other countries	35,042	52,605

We come now to the artificial production of nitrogen-bearing salts suitable for stimulating the growth of vegetation and will first consider those schemes for the direct fixation of the nitrogen of the air by which the nitrogenous fertilizers of the distant future will undoubtedly be supplied, and leave for later consideration the form of nitrogen salts, namely, sulphate of ammonia, the result of the dry distillation of organic substances; for undoubtedly the importance of ammonium sulphate as a fertilizer will greatly increase in the near future, gradually supplanting the waning supply of nitrates, and by reason of its much cheaper production postpone indefinitely the commercial fixation of nitrogen by electricity.

There is to-day no subject of chemical investigation of more vital importance than the fixation of nitrogen. It has already been accomplished on a small commercial scale by two different methods, but at a cost which probably is not sufficiently low to permit of successful competition with the present supply of nitrogen for fertilizer purposes, or for the manufacture of nitric acid. It was early determined by Wöhler and Deville that elementary silicon in contact with nitrogen resulted in a combination. Later it was found that boron, silicon, magnesium and titanium readily formed nitrides (convertible to ammonia with water) in an electrical furnace in an atmosphere of elementary nitrogen. Kaiser alternately leads nitrogen and hydrogen over magnesium hydride, producing ammonia, by the following reaction:

$$(3MgH + 3N = Mg_3N_2 + NH_3\ MgH_2 + 9H = 3MgH + 2NH_3.)$$

The commercial results of the experiments in these lines have been unsatisfactory.

As is well-known, the only processes which have attained results approaching success, are Dr. Frank's calcium cyanamide process, and Birkeland and Eyde's process of fixation by electric discharge.

In 1903, while in Berlin, at Siemen & Halske's laboratory, it was my good fortune to see Dr. Frank's apparatus and the various products which were the result of his first work in fixation of nitrogen, calcium cyanamide, dicyanamide, etc. From that time cyanamide experimentation has continued and the beneficial effect of calcium cyanamide as a fertilizer thoroughly demonstrated; while a considerable quantity has been produced a careful study of the process would show that as at present operated calcium cyanamide could hardly be produced in competition with nitrate or ammonium sulphate. Dr. Frank's first observation, greatly to his surprise, was that when using calcium carbide and nitrogen at high temperature he got calcium cyanamide instead of calcium cyanide as he had expected from his experiments with barium carbide in which he formed barium cyanide.

$$BaC_2 + N_2 = Ba(CN)_2.$$

With calcium carbide half the carbon was given off and he got calcium cyanamide.

$$CaC_2 + 2N = CaCN_2 + C.$$

Instead of first making carbide and passing nitrogen over calcium carbide at 900–1000°, the regular carbide process may be carried on in the presence of nitrogen and calcium cyanamide results. The most costly part of the process is the necessity of using nitrogen from which oxygen has been removed. This can be done only at considerable expense, either by passing over copper, or taking it from liquid air.

In arriving at a cost of calcium cyanamide which contains 16.5 per cent. available nitrogen, one must start with the cost of calcium carbide which at $20 per horse-power year is stated to be from $25 to $30 per ton. To this must be added the cost of the preparation of nitrogen free from oxygen and due allowance must be made for leakage and loss of this costly nitrogen. When all expense is carefully summed up, it is quite certain the cost per unit of nitrogen in cyanamide will be in excess of the cost of nitrogen in sulphate or nitrate.

In an address before the Chemical Congress recently held at Rome, Dr. Frank stated that while one electrical horse-power year would produce the necessary carbide for the binding of 772 kilos nitrogen, still in practice only about 300 kilos were fixed as cyanamide. He reiterates the necessity for cheap electrical power and refers to the Linde process for obtaining his liquid air and further suggests that, as by action of steam at high pressure on cyanamide he obtains ammonia, he can use the oxygen of the liquid air for oxidizing the ammonia to nitric acid, thereby obtaining this product more cheaply than by the Birke-

land and Eyde process. It has also been suggested that as the fixation of nitrogen proceeds more rapidly with an excess of oxygen in the air, the cyanamide and the Birkeland and Eyde process might be located together, the former taking the nitrogen, and the latter the oxygen of Linde's liquid air.

Other chemicals of much interest have been developed out of the experiments with calcium cyanamide which will doubtless be of considerable commercial value, namely, calcium dicyanamide, dicyandiamide, guanidine and its salts.

In a letter recently received from Dr. Frank he states that a separate company has been formed for the manufacture of calcium cyanamide derivatives, and that dicyandiamide will be on the market for use in explosives and for the hardening of steel.

It is nothing new to attempt the combination of nitrogen and oxygen to form nitric acid. Over 120 years ago Cavendish observed under influence of the electrical discharge the formation of oxides of nitrogen. Since 1893 this problem has again been vigorously attacked by Crookes, Lord Rayleigh, Nernst and others in the laboratory, and by the Atmospheric Products Co., of Niagara Falls, Kowalski in Switzerland, and Birkeland and Eyde in Norway, on a commercial scale. As is well known, the only method to achieve any considerable success is that of Birkeland and Eyde.

Dr. Otto N. Witt describes a visit to the Norwegian plant at Nottoden (*Chem. Ind.*, December 1st), and says the essential feature is that an electric arc is made to continually alter its path by the alternations of a powerful magnet. The gases from the furnace, containing only 2 per cent. nitrous gas, are very hot and must be cooled before going to the absorbing apparatus which is the same as in nitric acid works. A strength of acid equal to 50 per cent. is obtained. The heat of the gases leaving the furnace is utilized in making steam under boilers and in evaporating the solution of calcium nitrate. The weak gases are absorbed in towers of granite down which milk of lime passes.

According to Dr. Witt the Norwegian plant produces 1.5 tons daily and he states the yield to be 455 kg. 100 per cent HNO_3 (592 Kos. $Ca(NO_3)_2$) per kilowatt year, which he figures at the ridiculously low price of $4.00, whereas $16.00 would be more nearly the cost of power. Guye claims the yield per kilowatt year to be 500 kg. and the *Chemical News*, 650.

At a recent conference (*L'Echo des Mines et de la Métallurgie* 33, 1776, March, 1906, p. 379) of scientific and business men called together by M. L. Grandeau, chief of the French agricultural stations, Mr. Eyde was present and stated that since May 2, 1905, three furnaces of 500 kilowatts had been in run, each using 25 cubic meters of air per minute and that their calcium nitrate product contained 13 per cent. nitrogen and he gave 112 fr. ($22) as the cost of the power per ton of nitrate, assuming 15

fr. or $3 as the cost of a horse-power, absurdly low. If we assume the cost of power, $18, as attainable at Niagara Falls, the cost for power alone per kilo ton of calcium nitrate would be $132, containing 13 per cent. available nitrogen, as against $52 per ton for sodium nitrate containing 15 to 16 per cent. nitrogen, and $60 for ammonium sulphate, containing 21 per cent. nitrogen. Thus, unless electrical power can be obtained for $5 or $6 per horse-power year calcium nitrate cannot compete with ammonium sulphate as a fertilizer.

While the cyanamide at no very distant day may be produced commercially at such few places as can furnish power cheaply, the direct oxidation of the nitrogen of air by electric discharge I consider to be a problem far from being satisfactorily solved. It is endothermic, requiring 3.7 times the power that the exothermic cyanamide process does.

The suitability of calcium nitrate for fertilizer purposes is yet untried. Calcium cyanamide, on the other hand, has been thoroughly tested by many investigators and has been found to correspond closely in value to sodium nitrate and ammonium sulphate. L. Grandeau (*J. Agr. Prat.* No. 1, pp. 8–10 (1906)), in experiments with potatoes, showed the relative effectiveness of the three fertilizers to be sodium nitrate 100, ammonium sulphate 96.5, and calcium cyanamide 93.4.

While the cyanamide process or the nitric acid process may at some quite distant date be made commercially economical, yet the immediate supply of suitable nitrogen compounds to take the place of sodium nitrate is ammonium sulphate made first and in greatest quantity by gas houses and by by-product coke ovens, second by Mond producers, third, from the destructive distillation of peat and garbage.

The relative importance of sodium nitrate and ammonium sulphate to the fertilizer industry is shown by a comparison of the figures representing the production of the two salts. In 1905, the production of sodium nitrate amounted to 1,733,000 tons, of which 1,290,000 reached the soil as fertilizer, while the production of ammonia, figured as sulphate, of Great Britain, France, Belgium, Germany, Italy, Austria, Spain and the United States amounted to 557,000 tons, of which about 80 per cent. or 445,000 tons was used in fertilizers.

It is interesting to note that of the production of 557,000 tons of ammonium sulphate per annum, 44 per cent. was produced by Great Britain, 20 per cent. by Germany, 12 per cent. by the United States and 9 per cent. by France.

Another matter of interest is that of this 244,000 tons of ammonium sulphate produced in Great Britain per annum, 60 per cent. comes from gas works, 7 per cent. from blast-furnaces, 15 per cent. from shale plants, 10 per cent. from coke ovens, and 5 per cent. from Mond gas producers.

WORLD'S PRODUCTION OF AMMONIUM SULPHATE FOR 1905.

	Tons.
Great Britain	244,000
France	43,000
Belgium	39,000
Germany	115,000
Italy, Austria and Spain	48,000
United States	68,000

Great Britain's ammonium sulphate came from the following sources:

	1902. Tons.	1903. Tons.	1904. Tons.
Gas works	150,055	149,489	150,208
Blast-furnaces	18,801	19,199	19,568
Shale plants	36,931	37,352	42,486
Coke ovens	15,352	17,438	20,843
Gas producers	8,177	10,260	12,880

France's ammonium sulphate comes from:

	Tons.
Paris gas works	12,000
Provincial gas works	6,000
Paris sewage works	7,600
Provincial sewage works	3,500
Coke ovens	12,900
Shale	1,000

By what follows I hope to show that through the rapid extension of by-product coke ovens and the permanence of the industry, the waning supply of nitrogen due to the depletion of the nitrate deposits will be made good by ammonium sulphate, which is produced at the rate of 17 to 26 pounds for every ton of coal coked.

As long as coal lasts there will be a continually increasing production of ammonium sulphate. Foundries are located in large cities, blast-furnaces too are being constructed more and more in the neighborhood of cities which are not too far from the ore beds. Coke ovens will follow the blast-furnaces and in such location on the border of a large city the by-product coke oven can peform to the fullest extent its various functions.

A moment's consideration of the by-product coke oven and what it accomplishes will convince one that it is the foundation of an industry, now in its infancy, but destined to be chemically and metallurgically one of the most important and far-reaching industries in the domain of arts.

Its permanence as a source of nitrogen in a cheap form for fertilizer is assured by its underlying and fundamental importance in the operation of various industries. By it better coke, both for blast and foundry purposes, is produced than in bee-hive ovens. This is freely acknowledged by the best engineers in the country. A better price can be obtained from the foundrymen for by-product coke than for Connellsville because of its superior physical quality. This alone would insure the permanence of the

industry. But further, by it a superior quality of tar, the starting point for various industries rapidly becoming of importance, is produced in quantity varying from 60 to 100 pounds per ton of coal. The saturation of paper and felt with tar for roofing purposes is an industry of considerable importance. As a fuel in combustion engines by-product tar may be used as successfully as petroleum oil. Upon the products of the distillation of tar various industries are dependent. The utilization of pitch in the manufacture of briquettes is comparatively a new one in this country, but is destined to become of great importance, particularly to work up into valuable form the anthracite culm piles of Pennsylvania and the breeze of coke plants. Plants have recently been installed in Scranton, Detroit and Montreal for the manufacture of briquettes. Tar macadam roads, made with regular macadam foundation and an upper layer of three inches of a mixture of fine spawls and a certain grade of pitch, make a pavement perfectly impervious to moisture.

The distillate from tar has many uses, the most common being for the well-known purpose of creosoting railroad ties. Railroad men are convinced from long-continued experience that no other method of treating ties to preserve them is as satisfactory as creosoting with coal tar distillate which must have a high content of naphthalene. Large quantities are used for making lampblack. As the consumption of pitch for briquetting purposes increases, which requires the distillation at a high temperature, anthracene will be produced in large quantities and will be shipped to Europe for alizarine manufacture, and let us hope to find a market in this country for the same purpose.

One branch of the by-product coke industry thus far very little developed, but destined to be at some future time of immense importance, is the recovery of the aromatic oils of the gas.

Of the 10,000 cu. ft. of gas produced from a ton of coal, 6,500 cu. ft. are required in the coking process. This gas contains on an average 0.75 per cent. benzene and its homologues. Now the heat value of this gas is affected only slightly by the removal of benzene. By washing gas with petroleum or coal tar oil, a benzolized oil containing 2 to 3 per cent. of benzene is produced and by distillation a crude benzene light oil is obtained.

Only slight quantities of impurities, carbon disulphide, hydrogen sulphide, thiophene and naphthalene are found to be present, and purification and redistillation furnish a benzene 100 per cent. pure and suitable for nitrifying and converting to aniline.

What does this signify—what potentiality is here contained? The raw materials for all the aniline colors now imported into the United States are valued at millions of dollars. Formerly, it it could be said that the raw materials for a color industry were lacking in this country. This is no longer true. An abundance

of benzene is now available. How long before some enterprising company will take the initiative and on a considerable scale will undertake the manufacture of colors. As deterrents against the investment of capital in the color industry are offered on every hand: (1) lack in this country of competent chemists at low salaries, and (2) high price for labor, (3) the strong entrenchment of the business in the hands of the Germans, a business for which they have been peculiarly endowed. The close coöperation of the German teachers in chemistry with the manufacturer was admitted by Ostwald in an address while in this country to be the reason for Germany's control of the color industry. Our scientific schools are turning out chemists in large numbers and no one of our teachers is willing to admit they are not as well trained as the German chemists. The superior ingenuity of the American would soon devise machinery to displace labor; the raw materials, alkali and benzene, may be obtained at a lower price in this country than in Germany; nitric and sulphuric acids can be made as cheaply here as in Europe. There is no question but that under these conditions the aniline color industry, established with ample resources, after four or five years would return ample profits to the capital invested.

It is now about ten years since Mr. Fulton's comparison of Connellsville and Semet-Solvay coke in the Buffalo blast-furnaces dispelled all fears in the minds of metallurgists as to the suitability of by-product coke. Sir Lowthian Bell's statement of the loss of carbon in the upper part of the furnace was disproved.

A similar distrust came to gas manufacturers when it was suggested to them that by the coke oven equally good gas could be produced as by the gas retort. The recent installation of 120 ovens at Chicago, now supplying 3,000,000 cu. ft. of high candle-power gas to that city, in addition to plants of equal size at Milwaukee and Detroit, which have been in successful operation for more than two years, have now dispelled all the doubts of gas-makers as to the success of the by-product gas.

There is at present in the United States over 20,000,000 cu. ft. per day of illuminating gas enriched by benzene being furnished by coke ovens. It was supposed that in cold weather and under pressure coke oven gas enriched with benzene would lose much of its candle-power. An elaborate series of experiments on coke oven gas of an initial candle-power of 13 candles showed that this gas could be enriched to 24 candle-power and stand a temperature of zero, and a pressure of 20 pounds without appreciable loss. The experiments correspond closely to what calculations by vapor-pressure showed to be expected.

When one considers the operation of the coke oven when run as a producer of illuminating gas it is evident at once that it should produce gas superior to the ordinary coal gas made in the small gas retort. In the first place the higher temperature of the gas

retort tends to break down the illuminating series, benzene, into naphthalene. In the distillation of coal the gas richest in lighting properties is evolved during the early part of the process, the gas during the later period of distillation being poor in illuminants. Now all the gas from the gas retort rich and lean making a low average, is used, whereas in a coke oven only the rich gas, only that evolved during the first six hours, or one-fourth of the distillation period, is used for illuminating purposes, while the balance after giving up its benzene to the rich gas of the first six hours to make it richer, goes back to the ovens to effect the coking of the coal. It has been proved that gas of 15 to 16 candle-power can be made from coals not considered gas coals and of very low volatile matter by this selection method, and by addition of the benzene of the lean gas to the rich gas a candle-power of 19 to 20 is obtained.

As before stated, the amount of ammonia recovered varies from 16 to 27 pounds of sulphate per ton of coal, and is directly proportional to the percentage of volatile matter in the coal, a coal of 18 per cent. volatile matter yielding 16 pounds of sulphate, and one of 37 per cent. yielding 27 pounds. But this is a small percentage of the theoretical yield from the nitrogen of the coal. If all the nitrogen were converted to ammonia and recovered as such, the yield would be 133 pounds. But we find in the coke 48 per cent. of the original nitrogen.

While experimenting with certain Illinois coals it was found that the yield of ammonia was exceptionally high, and it was accounted for by the fact that the coal contained from 2 to 3 per cent. calcium carbonate. Lime will increase the yield of ammonia 20 to 40 per cent.

While a certain coal under one form of treatment, for instance, in the coke oven, yields 24 pounds of ammonium sulphate, the same coal under another treatment in Dr. Mond's producer at lower temperature and with steam returns 75 pounds of ammonium sulphate. The rapid construction of Mond-producer plants, particularly in England, will very largely increase our supply of nitrogen for the soil. Other nitrogenous substances are destined in the near future to add to our supply of ammonia, particularly as straight distillation results in such a large yield. I refer to the distillation of peat and to the distillation of garbage and other organic refuse. Peat in dry distillation yields 40 pounds, garbage 79 pounds of ammonium sulphate to the ton.

To recapitulate, we have as features of the by-product coke oven, which have been shown to be important as working toward its permanence and consequently as furnishing a permanent source of fertilizing nitrogen; (1) the production of coke superior to bee-hive coke; (2) the production of tar which enters so extensively into the arts; (3) it is furnishing the thus far-lacking material, benzene, in large quantities for the establishment of the color industry, but used until the establishment of this industry in

enriching gas for illuminating purposes; (4) it produces illuminating gas at a lower cost and of superior quality to that made in a gas retort; (5) it furnishes cyanogen equivalent to 1¾ pounds of potassium ferrocyanide per ton of coal; (6) as one of the by-products, it supplies the pyridine soon to be in demand for denaturing alcohol; (7) the hydrogen sulphide recoverable from the ammonia liquors when oxidized is sufficient to supply nearly one-half the sulphuric acid required in converting the ammonia into sulphate.

Therefore, let those take courage who have been predicting universal famine from lack of fertilizer nitrogen when the nitrate deposits shall be exhausted, for as long as our mines yield bituminous coal, by-product coke ovens will produce an ever-increasing amount of ammonia. As long as carbon in any form may be obtained, calcium cyanamide will carry nitrogen to the soil, and even after all carbon has been consumed, if only the rain continues to fall and rivers to produce water-power and hills give forth their limestone, and the earth is enshrouded with its nitrogenous atmospheric mantle, basic calcium nitrate, by the Birkeland process, will furnish the languishing vegetation with its necessary nitrogen.

SOLVAY PROCESS CO.,
SYRACUSE, N. Y.

A REVIEW OF THE AMERICAN PORTLAND CEMENT INDUSTRY.

BY RICHARD K. MEADE.

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Now that the United States ranks first of the Portland cement producing countries of the world, not only in point of the quantity manufactured but also with regard to quality, it seems fitting to take a look backward at the industry and see by what steps this success has been gained. First the enormous amount of engineering work now being done in this country has created a steady demand for Portland cement; second, the cheapening of the process of manufacture has allowed it to displace to a large extent other hydraulic cements, and also wood, stone and brick; third, the introduction of reinforced concrete, concrete building blocks, sewer pipes, etc., has widened enormously the field of concrete construction. All these causes have contributed to the wonderful growth of the Portland cement industry.

Few people realize how much concrete construction is done in the United States. If all the Portland cement made in this country last year had been used for sidewalks, these would have been equivalent to a sidewalk over 16 feet wide, reaching entirely around the world, at the equator. If this same cement

had been made into a solid cube of concrete, an edge of this would be three-sixteenths of a mile in length.

At the present time the Portland cement industry in America ranks second of the non-metallic industries in point of value, being exceeded only by the production of coal, oil and natural gas. It is entirely dependent upon the chemical profession for its existence and, indeed, gives employment to about 250 chemists.

At the present time there are approximately 90 Portland cement works in actual operation. According to the United States Geological Survey, these produced in 1905, 35,246,812 barrels of cement valued at $33,245,867. The enormous and rapid growth of the industry is shown by the fact that in 1880 only 42,000 barrels of cement were manufactured in this country, while last year's production was over 839 times this amount. The first Portland cement plant produced only 1,700 barrels a year, while one large modern cement plant claims a capacity of more than ten times this quantity daily.

The American Portland cement industry had its origin about 1874 when three small plants were started; one each in Pennsylvania, Michigan and Indiana. Roman, Rosendale or "Natural" cement had been made in this country since 1828, when cement rock (an argillaceous limestone) was discovered along the line of the Erie canal in New York. All the Portland cement used in this country prior to 1874 came from Europe, and chiefly from Germany and England.

In Pennsylvania, the Coplay Cement Co. was organized in 1866, to manufacture natural or Roman cement at Siegfried, Northampton Co. A few years later the manager of this company, Mr. David Saylor, as the result of experiments, became convinced that Portland cement could be manufactured from the rocks of his quarry, and after many trials and some failures and discouragements his company began the manufacture of Portland cement in 1875, and has been a continuous producer ever since. About 1871 Mr. Thomas Millen and his son, Duane Millen, began manufacturing cement sewer pipe at South Bend, Indiana, importing English Portland cement for the purpose. Their attention was called to the probability of manufacturing Portland cement from the marls and clays found around South Bend by a former employee of the English firm of Portland cement manufacturers, Knight, Bevan and Sturge, of Northfleet. They, thereupon, began investigations which led them to establish a plant at South Bend sometime about 1875. In 1872 a small plant, called the Eagle Portland Cement Co., was started at Kalamazoo, Mich., by Chicago capitalists. Plants were also built at Wampum, Pa., at Rockport, Me., and in the Rosendale District of New York, prior to 1880. Of these three plants, however, only one, that at Wampum, was at all successful. The Eagle Portland Cement Co. also failed. Of the six plants mentioned only one has achieved

any marked success, namely the Coplay Cement Company, which is now a large manufacturer.

Other Portland cement plants which were established before 1890 are the American at Egypt, Pa. (near the Coplay); the Empire at Warners, Onondaga County, New York; the Buckeye at Harper, Logan County, Ohio; and the Western at Yankton, South Dakota.

Portland cement is now manufactured in this country from the following raw materials—cement rock and limestone, limestone and clay or shale, marl and clay, and limestone and blast-furnace slag. In 1905, 52½ per cent. of the Portland cement manufactured in this country was made from cement rock and limestone, 36½ per cent. from limestone and clay or shale, and 11 per cent. from marl and clay. The manufacture of cement from cement rock and limestone is distinctly an American process, but both limestone and clay, and marl and clay have been used for this purpose abroad.

Cement rock is an argillaceous limestone found in a narrow belt, extending in a northeasterly direction through the counties of Berks, Lehigh and Northampton in Pennsylvania and Warren County in New Jersey. The deposit is about 50 miles long and is nowhere more than four miles wide. Cement rock contains from 65 to 80 per cent. carbonate of lime and from 15 to 25 per cent. silica, oxide of iron and alumina taken together.

The early cement plants using clay and marl or limestone and clay all followed closely the European practice of cement manufacture, which consisted in finely grinding a wet mixture of marl and clay or limestone and clay and then moulding the mixture into bricks, which were burned in some form of upright kiln. Those plants using cement rock and limestone, however, found it impossible to get the fine crystalline mixture to cohere sufficiently to form briquettes which could be handled without crumbling. At the Coplay Cement Co's. plant, therefore, a small percentage of cement was added to the mixture as a binder, while at the American Cement Co's. plant at Egypt, coal tar was used for this purpose. The use of cement rock as a raw material and the employment of coal tar as a binding material constituted the first advancement of American over European practice.

The machinery for grinding both the raw material and the cement clinker at these early cement mills was very primitive. Mill stones, such as are used for grinding flour in the small water-power mills with which we are all familiar, were used to grind both the clinker and the harder raw materials while edge runner mills were used to grind clay and marl. As the output of these early plants increased the need of more efficient grinding machinery also grew, and ball and tube mills were imported from Europe and used for grinding both the clinker and the raw materials. Several distinctly American forms of grinders were also intro-

duced in the early eighties. The Gates gyratory crusher was found to be best suited to the crushing of hard material, such as limestone and cement rock, preparatory to its final reduction by other means. The Griffin mill was introduced into the plant of the American Cement Company at Egypt, Pa., in 1885, and soon became a very popular mill. The Atlas Cement Company about the same time installed a somewhat similar type of pulverizer, the Huntington mill, the use of which never became general, however. Of recent years two new forms of fine grinders have been introduced—the Kent mill and the Fuller Lehigh mill. The Edison Portland Cement Company uses a system of fine grinding peculiar to itself, consisting of rolls followed by air separators, the idea of the well-known American inventor, Thos. A. Edison.

At the present time mill stones have been entirely done away with except at one or two small mills, and practically all the grinding is now done by one of the following systems:

FOR GRINDING LIMESTONE AND CEMENT ROCK.

I.	II.
(1) Gates crushers.	(1) Gates crushers.
(2) Ball mills or comminuters.	(2) Rolls.
(3) Tube mills.	(3) Griffin mills or Lehigh mills.

FOR GRINDING PORTLAND CEMENT CLINKER.

I.	II.	III.
(1) Ball mills.	(1) "Pot" crushers.	(1) Kent mills followed by air or screen separators.
(2) Tube mills or comminuters.	(2) Rolls.	
	(3) Griffin mills.	

The cement mills built prior to 1890 all used upright kilns similar to those used abroad. Some of these represented the most improved forms. The Coplay used the Schoefer kiln, the Buckeye employed the Dietsch kiln and the Western installed the Johnston kiln. These kilns were economical with respect to fuel but very costly as regards labor. A rotary kiln had been invented by an English engineer, Ransome, in 1885 but had never been successfully used there. The Atlas Portland Cement Company became interested in this form of kiln and installed it in the plant they built in 1888 at Northampton, Pa. After much experimenting they succeeded in operating this form of kiln successfully. The upright kilns all required the raw materials to be moulded into bricks which were fed into the kiln alternately with layers of coke or other fuel. With the rotary kiln on the other hand the fine material could be fed into the kiln in the form of a powder, thereby saving much labor. The clinker from the upright kilns is also very unevenly burned, necessitating hand-sorting to remove the underburned portions. The clinker from the rotary kiln on the other hand is very uniformly burned and requires no sorting.

The rotary kiln, though an English invention, has been developed and made practical entirely through American brains,

Seaman, Hurry and Navarro being chiefly connected with the making of its success. Shortly after the utility of the rotary kiln upon dry materials had been proved, S. B. Newberry, formerly a professor of chemistry in Cornell University, adapted it to use with wet materials, pumping the mixture of clay and marl, containing 50 to 60 per cent. water, directly into the kiln.

Ransome heated his kiln by means of producer gas, but oil was generally used in this country until about 1899 when burning with powdered coal was introduced. This latter is now generally used for burning, except in sections where oil or natural gas is cheap.

At the present time, practically all the cement manufactured in this country is burned in rotary kilns. They have also been introduced extensively abroad and probably in the next ten years will displace other forms of kilns even in Europe.

As installed up to a few years ago rotary kilns were usually made 60 feet long and 6 feet in diameter. These kilns were found to be wasteful of fuel, as over 45 to 60 per cent. of the fuel energy was lost in the fuel gases and another 10 to 15 per cent. in the hot clinker.

At the present time two methods are being experimented with for the saving of the heat in the kiln gases.

(1) Lengthening the kiln, thereby giving greater time for the material to absorb the heat of the kiln gases.

(2) Passing the gases of the ordinary short kiln through an upright boiler and then through an economizer.

Thomas A. Edison is the chief exponent of the long kiln, as those in his plant at Stewartsville are 150 feet long. These kilns were put in operation in the fall of 1903 and proved entirely practical and effected the economy in fuel which the inventor had promised they would. His experiment was watched with great interest, and, as soon as the success of these mammoth kilns was known, several of the mills, then under construction lengthened their kilns to 80 feet. This plan has also been tried by some of the older mills who extended their kilns to from 100 to 140 feet. Several of the mills now being built are erecting 100, 125 and 140-foot kilns.

The attempt to utilize the heat of the kiln gases under boilers was first made, I believe, at the plant of the Nazareth Portland Cement Co., but after encountering many difficulties, the plan was abandoned and the boilers taken away. Prof. R. C. Carpenter, of Cornell University, however, has successfully tried this plan at the plant of the Cayuga Lake Cement Co., and also at that of Kosmos Portland Cement Company.

A number of devices have been patented, designed to utilize the heat carried off by the clinker. None of them is used to any extent. A rotary cooler below the kiln through which the clinker

passes and through which the air for combustion is drawn by the kiln draft seems the simplest and most feasible device.

The improvement in the quality of cement has been as marked as the improvement in the process of its manufacture. General Gilmore, in a test made of the Eagle Portland cement, in 1876, found its strength to be less than 300 pounds per square inch after seven days, while to-day cements having a seven-day neat strength of 700–800 pounds are the rule and not the exception. Some of this improvement is no doubt due to the increased efficiency of grinding machinery and it is now an easy matter to obtain a cement 95 to 96 per cent. of which will pass a No. 100 test sieve.

American cement technologists have also made some very noteworthy contributions to the scientific literature of cement. Perhaps the most extensive investigations undertaken by an American chemist are those detailed by Mr. Clifford Richardson in his numerous papers on the chemical constitution of Portland cement. His investigations are perhaps the most interesting of any of the numberless attempts to solve the riddle of what is Portland cement and what gives it its binding properties. Another investigation made some ten years ago along the same line was that of Spencer B. and Wm. B. Newberry, Prof. A. V. Bleininger has also investigated the composition of Portland cement. While the volume of work done upon this subject in the United States is not as large as that published by German scientists, what has been done here is of probably just as high a grade as that carried out in Europe, in spite of the distinction of some of the foreign investigators. Prof. E. D. Campbell has carefully experimented to find out the influence of the ratio of lime to silicates and also of fine grinding of the raw materials upon the clinkering temperature. Richards, Soper and Carpenter all measured the thermal efficiency of rotary kilns. Richards investigated that of a 60-foot kiln, Soper that of one of 100 feet and Carpenter that of a kiln whose waste gases were used to fire a boiler. W. B. Newberry investigated the regularity of burning a 60-foot kiln and Meade proved the loss of alkalies and sulphur in burning. He also showed the contamination of the cement by the fuel ash to be smaller than it had generally been considered. Carpenter investigated the substitution of calcium chloride for gypsum to retard the setting time of cement and Meade and Gano showed that calcium sulphate in any form could be used for this purpose. In addition to the above more important papers, the technical press has contained frequent articles upon cement manufacture by Newberry, Lathbury, Spackman, Lesley, Carpenter, Eckel, Meade, Lewis and Lundteigen. Three books dealing exclusively with Portland cement manufacture and two others largely devoted to the subject have also been published. Four trade papers are now devoted exclusively to cement

technology and the uses of cement and many valuable papers have been published in these.

On the physical testing of cement the work done in this country has been excellent. In the early eighties the American Society of Civil Engineers appointed a committee to investigate the subject of cement testing. This committee reported in 1885. Later another committee was appointed which reported January 21, 1903. This report was amended January 20, 1904, and the methods of test recommended by it are now considered the standard ones.

The American Society for Testing Materials turned its attention to the drafting of uniform specifications for cement and its committee reported June 17, 1904. This set of specifications was endorsed by the American Institute of Architects, the American Railway Engineering and Maintenance of Way Association, the Association of American Portland Cement Manufacturers and the American Society of Civil Engineers and may hence be considered the standard specifications.

The following are noteworthy examples of individual efforts along this line. Porter investigated the lack of uniformity in cement testing. Maclay, Lundteigen, Lewis and Taylor made a study of the accelerated tests for constancy of volume. Lazell showed the lack of uniformity in standard sieves. Meade proved the sieve test to be inadequate for determining fineness in cements ground by different processes. Taylor investigated the influence of aeration on specific gravity. Spaulding, Jamison, Meade and Taylor have published treatises upon the subject of cement testing.

Much improved apparatus for testing cement has also been perfected in this country. Jackson and McKenna have both devised apparatus for determining specific gravity. Gilmore's needles were for a long time used for testing the setting time of cement, and now that the Vicat apparatus has been recommended Bramwell has simplified this. The Fairbanks Co. manufactures an improved form of testing machine which is much used and possesses many points of advantage over its standard German counterpart, the Michaelis machine. Olsen and Riehle have also brought forward excellent testing machines which are much used in this country.

Much has also been done on improving methods of analysis. The New York section of the Society of Chemical Industry appointed a committee to investigate the subject as did also the Lehigh Valley section of the American Chemical Society. Both committees reported and advised methods of analysis. The New York section committee reported a somewhat long but very accurate scheme of analysis, while the Lehigh Valley section committee attempted merely to unify the existing methods and eliminate the seriously objectionable features from these. Both

reports embodied much research work, painstaking investigation and laborious correspondence, and while probably neither method is extensively used just as published, the agitation over the matter accomplished much. Hillebrand's valuable paper upon silica determinations also threw much light upon the subject. The rapid determination of lime in raw materials is now largely made in this country by the method of solution in standard acid and titration of the excess of the latter with standard alkali. It has been found quicker and more reliable than the one of measuring the volume of carbon dioxide liberated, so largely used in Europe.

Newberry's method of determining magnesia by precipitation with a known volume of standard caustic soda is also much used as is Jackson's photometric method for sulphur. In 1901 the writer published his book on the "Chemical and Physical Examination of Portland Cement" which was the first book in any language treating to any extent of the analysis of Portland cement and its raw materials. Frequent papers upon the subject of cement analysis have also been published by W. B. Newberry, Hillebrand, Peckham and the writer.

NAZARETH, PA.

NOTES ON THE USE OF PEAT.

BY CULLEN W. PARMELEE.

Received July 9, 1906.

THE purpose of this paper is to review certain phases of the peat industry which are of especial interest to the agricultural chemist. As we know, the industry in all its various forms is of great antiquity on the continent of Europe and at the present time peat is being studied systematically at government experiment stations, a considerable periodical literature is devoted to the matter and there are a number of societies interested in developing its uses. In this country the industry has never flourished heretofore, chiefly for economic reasons. Of late, however, interest in the matter has been growing, and it will probably be only a short time before we give peat the same amount of serious study that it is having elsewhere.

The first point to which I would call your attention is the importance of the recovery of swamp land. Parsons, in a recent bulletin published by the New York State Geological Survey, states that "it is estimated that one-twentieth of the area of that state is swamp land" and he points out that unimproved land is assessed at about $5 per acre and the drained land sells ordinarily at $200 to $500. A similar condition undoubtedly exists in all our northern states to a greater or less degree. The practical value of this is twofold; first, the possibility of increasing the taxable wealth; second, recovering the cost of draining by utilizing

the peat removed. Similar work is done in Holland with the result that peat is the common fuel.

With respect to the usefulness of peat for agricultural purposes, the past forty or fifty years has seen a very decided change in views. In 1866, Dr. Samuel Johnson produced his very interesting book on "Peat and Its Uses." It was founded upon his observations and experiments, and his conclusions were based upon the knowledge of agricultural chemistry as understood at that time. During the years which have passed, this branch of chemistry has developed marvelously, and we cannot accept in their entirety the opinions which he gave then. For instance, with the abundance of cheap concentrated fertilizers at hand it would be foolish now to attempt to use peat as a fertilizing material. The labor of digging and spreading material having from 70 per cent. to 80 or 85 per cent. water would be too costly and the time necessary for it to become effective would be too long. In isolated communities under certain favorable circumstances it may be permissible but not otherwise.

The most important use of peat as far as the agriculturist is concerned is undoubtedly its use as litter and subsequent use as compost. Of course, not all varieties of peat are available. Only the soft fibrous material, free from lumps can be used. At present a considerable quantity is used in this country in large stables such as those of breweries, department stores, etc. We import almost all, getting it from Holland. In this country there is only one plant producing peat litter and this is located in Indiana. Not all peat litter has equal absorptive power but a good sample will absorb eight times its own weight of urine while straw absorbs only three times its weight. Moreover, peat has the advantage of preventing decomposition and loss of ammonia. As a compost material, the litter has not only the advantages named but also that of possessing a considerable nitrogen content, which, of course, is increased by that absorbed as a bedding. These matters have, however, been emphasized by other writers who give greater detail than is here necessary. I merely wish to repeat it in order to draw attention to a neglected opportunity.

A method of utilization which is at present finding considerable development is the employment of powdered peat as a filler in fertilizers. For this purpose the earthy varieties of peat are available. Here it serves the purpose of preventing the formation of lumps or crusts of hygroscopic materials. The fertilizer is consequently more easily spread. At present there are three factories operating in New Jersey and one in Illinois and possibly others elsewhere. Besides this use it is said to be used as a diluent for the preparation of low-grade dried blood.

The question naturally arises, what valuation is to be allowed for the nitrogen so introduced? It is quite unlikely that the peat

is used primarily for the nitrogen it contains, but it is there and should be differentiated from the other more available forms. Regarding this point there seems to be a wide divergence of opinions among certain authorities. Stutzer ("Die Behandlung und Anwendung des Standdüngers") says that the nitrogen of peat has no value because of the long interval of time required to render it available. Storer, in his book on agriculture, recognizes its comparative inertness but states "that it is a matter of familiar observation and experience that the peat nitrogen may be made to contribute to the support of crops and that it has consequently a considerable money value." He also quotes Nessler as follows: "Although the nitrogenous constituents of peat decompose in the soil more slowly than the altered ossein in meal from steamed bones they do nevertheless in some cases decompose more quickly than the nitrogenous components of wool, or than the ossein in coarse meal from raw bones or than those in leather meal, either that or from torrified leather."

As to the quantity of nitrogen to be found in peat, Dr. Johnson reports that he found upon the examination of thirty samples from Connecticut an average of 1.5 per cent. with a maximum of 2.9 per cent. In the course of a study of New Jersey peats, 123 samples have been examined in my laboratory. The nitrogen has ranged from 0.74 per cent. to 2.83 per cent. with an average of 1.75 per cent.

RUTGERS COLLEGE,
NEW BRUNSWICK, N. J.

NEW BOOKS.

ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By HARRY C. JONES, Professor of Physical Chemistry in Johns Hopkins University. New York: D. Van Nostrand Co. 1906 viii+212 pp. Price, $2.00.

The author states that the contents of this book had been published previously, as a series of articles, in the *Electrical Review;* the present work is a revised edition of these articles. "The aim of the writer has been to present the more important facts and conclusions in connection with the work on the electrical nature of matter and radioactivity as far as possible in non-mathematical language. * * * While the work is written in semi-popular style, the attempt has been made to treat the subject with scientific accuracy." A perusal of the book shows that Professor Jones has accomplished very satisfactorily the objects announced in the preceding lines quoted from the preface.

The first four chapters deal with the electrical conductivity

of gases, the nature of the electrons constituting the cathode rays, and the evidence of the electrical nature of matter. In the fifth chapter, X-rays and Becquerel or β-rays, and the identity of the latter with cathode rays are discussed. The next six chapters treat of the discovery of radium and of the phenomena of radioactivity. These are followed by three chapters on radioactive emanations and induced radioactivity. The concluding four chapters deal chiefly with the spontaneous transformation of matter and the explanation of the phenomena of radioactivity by means of the disintegration hypothesis and the electron hypothesis regarding the nature of the atom.

There are numerous references to the original literature, but no attempt has been made at completeness in this direction. There is a good index. A few misleading or erroneous statements exist. On p. 141 it is stated that after the separation of UX, the remaining uranium was not appreciably radioactive. This is of course true if the activity is measured photographically, but electrical measurements show that the ionizing power of uranium is but slightly altered by the removal of UX. On p. 147 it is stated that thorium precipitated three times by ammonia is only about one one-hundredth as radioactive as ordinary thorium; the correct statement is found on p. 193. The book is well up-to-date and includes discussions of much of the most important work of the year 1905. It will give the general reader an adequate idea of the nature of the most important achievements in this field of science. It will also serve as a good introduction to the advanced treatises of J. J. Thomson and of Rutherford and to the original literature, for those who wish to study the subject thoroughly.

H. N. McCoy.

LECTURE-NOTES ON CHEMISTRY FOR DENTAL STUDENTS. By H. CARLTON SMITH, PH.G. New York: John Wiley & Sons. 1906. viii+273 pp. Price, $2.50.

This course in dental chemistry includes the following subjects: Qualitative Analysis, Dental Metallurgy, Volumetric Analysis, Microchemical Analysis, Organic Chemistry, Physiological Chemistry, Digestion, Urine. If the students of the Harvard Dental School, for whom the course was prepared, have found it sufficient for their needs, they must be made of better stuff than ordinary students. For if the latter were reasonably familiar with elementary general chemistry, it seems clear that only the

most intelligent of them could profit by the brief treatment, which some of these topics receive. The sections on organic and physiological chemistry are painfully concise.

It is doubtless convenient to have in concise form "the data that are most likely to be of use in practical work," but students should have more than this. In the chapter on dental metallurgy is found much interesting information regarding alloys, amalgams, cements, solders, etc. In another chapter many local anesthetics are described. Nine half-tone plates with 54 figures of the crystals and the other bodies most likely to be found in microchemical study of the saliva, the urine, mouth-washes, and other substances of interest to dentists, should be of value to student and practitioner alike. L. B. HALL.

CONGRESS OF ARTS AND SCIENCE, UNIVERSAL EXPOSITION, ST. LOUIS, 1904. Edited by HOWARD J. ROGERS, A.M., LL.D., Director of Congresses. Volume IV: Physics, Chemistry, Astronomy, Sciences of the Earth. Boston and New York: Houghton, Mifflin & Co. 1906 x+766 pp. Price, $2.50 net.

The addresses presented before the Congress of Arts and Science at St. Louis, are being published in eight volumes, of which Vol. I contains the addresses on the subject of philosophy and mathematics and Vol. IV the addresses of most interest to chemists and physicists. Vol. IV contains the following addresses: The Unity of Physical Science, R. S. Woodward. The Fundamental Concepts of Physical Science, E. L. Nichols. The Progress of Physics in the Nineteenth Century, Carl Barus. The Relations of the Science of Physics of Matter to Other Branches of Learning, A. L. Kimball. Present Problems in the Physics of Matter, F. E. Nipher. The Ether and Moving Matter, D. B. Brace. The Relations of Physics of Electrons to Other Branches of Science, Paul Langevin. Present Problems of Radioactivity, Ernest Rutherford. On the Fundamental Conceptions Underlying the Chemistry of the Element Carbon, J. U. Nef. The Progress and Development of Chemistry during the Nineteenth Century, F. W. Clarke. Inorganic Chemistry—Its Relations with the Other Sciences, Henri Moissan. The Present Problems of Inorganic Chemistry, Sir William Ramsay. The Relations of Organic Chemistry to Other Sciences, Julius Stieglitz. Present Problems of Organic Chemistry, W. A. Noyes. The Relations of Physical Chemistry to Physics and Chemistry, J. H. van't Hoff. The

Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory, A. A. Noyes. Problems in Nutrition, Otto Cohnheim. The Present Problems of Physiological Chemistry, R. H. Chittenden. The last half of the volume contains six papers upon astronomical subjects and sixteen papers upon sciences of the earth. W. A. N.

FOOD AND NUTRITION. LABORATORY MANUAL. By MISSES BEVIER AND USHER, Household Science Department, University of Illinois. 1906–1907. 45 pp. Price, $1.00.

The book is essentially a set of brief laboratory directions dealing with the chemical properties of the "proximate principles" and organic compounds which accompany them in the common foods. It also touches very briefly upon some of the processes of digestion. The successful use of the manual certainly presupposes a fairly comprehensive acquaintance with several of the biological sciences—an experience more extensive than is usually accorded to students of household economics.

The most serious criticism, perhaps, applies to the selection of subject-matter for discussion. Some of the text involves controversial questions (*e. g.*, the adequate classification of proteids) which must at most have a very superficial value. Additional topics (*e. g.*, the chemistry of purins) might advantageously have been included because of their peculiar significance in nutrition. The digestion of fats also deserves mention in a course which presents lecithins and fats in some detail, and considers the other familiar types of enzyme action.

The authors deserve credit, however, for attempting to indicate the broad applications of physiological chemistry to the problems of daily life. LAFAYETTE B. MENDEL.

LABORATORY MANUAL OF GENERAL CHEMISTRY. By THOMAS EVANS AND J. F. SNELL. Fourth Edition. University Press, University of Cincinnati, Cincinnati, Ohio. 1905. 8vo. 70 pp. Price, 50 cents.

This laboratory manual contains twenty-nine practice exercises on the non-metallic elements and compounds and eighteen on the metals. The directions for making the experiments are carefully written. A few quantitative experiments are brought in quite early in the course. These are: measurement and reduction of gas volumes, definite and multiple proportions, synthesis of water, weight of a liter of oxygen and the equivalent weight of zinc.

Some of the more salient properties of solutions, such as saturation, supersaturation, ionization and hydrolysis, are illustrated qualitatively. The experiments illustrating mass action are well selected and with accompanying lectures by the instructor can not fail to give the student a good idea of this subject. Additional questions requiring reasoning and study on the part of the student would have been an improvement. Taking it altogether, however, the newer views as well as the older descriptive facts are illustrated and the course as outlined is a very good one for beginners in chemistry. EDWARD H. KEISER.

LABORATORY EXPERIMENTS TO ACCOMPANY OUTLINES OF INORGANIC CHEMISTRY. By FRANK AUSTIN GOOCH AND CLAUDE FREDERIC WALKER. New York: The Macmillan Co. 1905. 29+104 pp. Price, 50 cents.

The experiments in this laboratory manual are divided as the text-book which it is to accompany into two parts, one inductive and the other descriptive. In the first or inductive part, which consists of 29 pages, there are given experiments to illustrate chemical change, elements and compounds, chemical equivalents (four quantitative experiments), hydrogen, oxygen and oxides, water solution, hydration and hydrolysis, air and nitrogen, electrical equivalents and ions, acids, bases and salts, action and equilibrium.

In the second or descriptive part the elements are taken up in groups according to the periodic system of classification. The chief properties of each element are shown by qualitative experiments. There are constant references to the text-book for equations and explanations.

Taking the book as a whole, it contains a very good course in descriptive chemistry, and the student taking this course will, if he has a good memory, learn many facts concerning the elements and compounds and he will have had good practice in writing reactions. There are, however, very few questions asked him and he can get all his explanations in the text-book. There is nothing to make him think and reason. It would have been an improvement if he had been made to reason out the connection between the facts that he observes in the second part and the laws and principles of the first part. EDWARD H. KEISER.

RECENT PUBLICATIONS.

LEHRBUCH DER PHYSIOLOGISCHEN CHEMIE IN 30 VORLESUNGEN. By Emil Abderhalden. Wien: Urban & Schwarzenberg. 1906. VII+787 pp. Marks 18. Geb. in Halbfrz., Marks 20.

GRUNDRISS DER PHARMAKOLOGIE IN BEZUG AUF ARZNEIMITTELLEHRE UND TOXIKOLOGIE. By O. Schmiedeberg. Fifth edition. Leipzig: F. C. Vogel. 1906. XII+574 pp. Marks 11.50. Geb., Marks 12.75.

TECHNOLOGIE DER CYANVERBINDUNGEN. By Wilhelm Bertelsmann. Müchen: R. Oldenbourg. 1906. XII+332 pp. Marks 10.

ANLEITUNG ZUR CHEMISCHEN UNTERSUCHUNG DES WASSERS AUF SEINE BRAUCHBARKEIT FÜR DEN MENSCHLICHEN GENUSS, ZU GEWERBLICHEN ZWECKEN, ETC. By O. Linde. Second edition. Göttingen: Vandenhoeck & Ruprecht. 1906. VI+62 pp. Marks 2.

DIE NORDDEUTSCHE KALIINDUSTRIE. By H. Precht. Stassfurt: R. Weicke. 1906. III+62 pp. Marks 2.25.

CHIMIE PHARMACEUTIQUE MINÉRALE. By Blas et Ranwez. 2e fasc. Metaux. Paris: O. Doin. VIII+430 pp. 20 fr.

KURZES REPETITORIUM DER ORGANISCHEN CHEMIE. FÜR STUDIERENDE BEARB. By Kurt Dammann. Freiburg i/B. Herder. 1906. XIII+256 pp. Marks 4. Geb., Marks 4.50.

UNTERSUCHUNGEN ÜBER RADIOÄKTIVE SUBSTANZEN. (VI. MITTEILG.) ÜBER RADIUM F. (POLONIUM). By Stef. Meyer & Egon Ritter v. Schweidler. Wien: (A. Hölder). 1906. 26 pp. Marks 0.95.

ANLEITUNG ZUR QUALITATIVEN ANALYSE. By Ernst Schmidt. Edition six. Halle: Tausch & Grosse. 1906. IV+95 pp. Marks 2.80.

UNTERSUCHUNGEN ÜBER AMINOSÄUREN, POLYPEPTIDE UND PROTEÏNE. (1899-1906). By Emil Fischer. Berlin: J. Springer. 1906. 10+770 pp. Marks 16. Geb. in Leinw., Marks 17.50.

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A GLOSSARY OF SILK TERMS. New York. American Silk Journal (1905). 24 pp. $0.25.

TRAITÉ MÉTHODIQUE DE LA FABRICATION DES ENCRES ET CIRAGES, COLLES DE LA BUREAU, CIRES À CACHETER: 300 FORMULES. By A. F. Gouillon. Paris: Garnier frères. 4 fr. 50.

LE CAOUTCHOUC EN INDO-CHINE, ÉTUDE BOTANIQUE, INDUSTRIELLE ET COMMERCIALE. By C. et A. Spire. Paris: A. Challamel. 18 fr.

MANUEL PRATIQUE DE LA FABRICATION DES EAUX ET BOISSONS GAZEUSES. By J. Fritsch. Paris: H. Desforges. 188 pp. 3 fr. 50.

La Production Électrique de l'Acide Nitrique avec les Elements de l'Air. By L. Grandeau. Paris: Berger-Levrault et Cie. 64 pp. 2 fr.

Le Blanchissage et l'Appret du Linge. By L. Vérefel. Paris: Ch. Béranger. 3 fr.

Elements of Chemical Engineering. By J. Grossmann. Pref. by Sir William Ramsey. London: Griffin. 1906. 160 pp. 3/6.

Glues and Cements. Handbook on Adhesives and Fillings for Workshop Use. By H. J. S. Cassal. London: L. U. Gill. 1906. 120 pp. 1/.

Testing Milk and Milk Products. By Lucius L. Van Slyke. New York: D. Van Nostrand. 1906. 190 pp. $0.75.

Influence of Molecular Constitution upon the Internal Friction of Gases. By F. M. Pedersen. (Thesis.) New York: D. Van Nostrand. 1906. 59 pp. $0.50.

Treatise of Practical Brewing and Malting. By F. Thatcher. London: D. Van Nostrand. 1905. 560 pp. $8.50.

Chemistry and Technology of Mixed Paints. By Maxmilian Toch. New York: D. Van Nostrand. 1906. $3.00.

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Hints on Painting Structural Steel and Notes on Prominent Paint Materials. By Houston Lowe. Dayton, Ohio: The Lowe Bros. Co.